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URANIUM and ATOMIC POWER

*A COMPREHENSIVE PRACTICAL AND THEORETICAL
EXPOSITION OF THE URANIUM MINERALS, BASED ON
THE CHEMISTRY OF URANIUM, AND INCLUDING THE
POSSIBILITIES OF ATOMIC POWER*

By

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Fluorescent Light and Its Applications, etc.*



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CHAPTER

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PREFACE

—EVER since its discovery uranium has been associated with the great events in science. Uranium has been the “water boy” for the spectacular plays in chemistry and physics. For some years the element was forced into comparative obscurity by the acclaim for radium and X-rays. But now uranium has come into its own. With the recent developments in nuclear fission the future of uranium has been accorded an extremely bright outlook. —

Uranium is now on a road which may eventually be surpassed by few elements in terms of service to humanity. At present uranium 235 holds the greatest possibilities as a future source of atomic power. The separation of uranium 235 from the other isotopes is already a laboratory fact, but much remains to be done to develop this fact into commercial realization. Many physicists believe that atomic power may be obtained from uranium in the near future. Others hold to the premise that such an accomplishment is still in the distant future or may never come to pass. It is the opinion of the present writers that the gravity of evidence now at hand should favor an optimistic outlook.

We have endeavored to discuss the subject of uranium mainly from a chemical standpoint. If we are vague on some phases of presentation, or if the information appears to be scant, we ask you not to excuse this. To ask you to overlook scantiness of knowledge in portions of our work would imply that we believe the study of uranium and its minerals is mature. We believe that the study of uranium minerals is more on the order of an adolescent who requires the directive efforts of those more experienced.

In our treatment of the chemistry of uranium we have endeavored to present unusual facts pertinent to our subject. The procedures for estimation and detection of uranium are

described in several following chapters. Here, additions may be made to the field by completeness of scope, as well as by presentation of some of the original studies of the present writers.

Since the cyclotron and similar apparatus used in analysis and synthesis of atomic species has been brought into prominence, considerable speculation has accompanied regarding the possibilities of atomic power. The present problem appears to hinge upon the separation of uranium 235—an isotope which exists in all uranium minerals—in sizeable quantities. Perhaps uranium 235 may be termed “A Fuel of the Future.” The possibilities of atomic power are discussed in a separate chapter.

In compiling the data on the uranium minerals we have been impressed by the striking similarity between numerous species. We believe it altogether probable that species of some rare uranium minerals, the properties of which have been described from only limited amounts of specimen material, may prove identical with previously described species if subjected to modern methods of X-ray spectrographic analysis.

The completeness of the bibliography varies. Sections which refer to chemical methods are not as extensive as those in which minerals are listed. In the latter an effort has been made to give the original or an early reference for the species described. More complete information about atomic physics can be obtained from the several texts available on the subject.

It will be noted that in the chemistry of uranium many of the papers can be considered obsolete. This indicates the period when most of the reconnaissance work on the compounds of uranium was performed. Even familiar names like J. J. Berzelius will be noted. This also indicates the relatively small number of studies which have been conducted

recently on the new compounds of uranium. A large number of extensive descriptions of the compounds of uranium are difficult to find, being restricted more to the few comprehensive treatises on theoretical inorganic chemistry. Moreover, only a comparatively small number of organo-uranium compounds are described as such in the literature.

We do not consider the chemistry of uranium to be as complete as some of the literature leads one to believe. This is evident from the fact that we have presented a number of complex uranium salts in terms of R and X, the values for known members of specific series being given. Hence, we believe that the values for R and X may be extended considerably by additional investigation.

We believe that we are treating some of the fundamentals of a new science which includes, but which does not entirely consist of, the rapidly vanishing borderline between chemistry and physics. We also believe that we have described what may be the groundwork of a future industry, the possibilities of which are fantastic to many, but not too highly improbable to those with a mind to progress.

We have purposely included material of a controversial and thought-provoking nature. This has many apparent values. Finally, we are indeed aware of the numerous and exceptionally argumentative aspects characteristic of our subject. It is sincerely hoped that certain original presentations herein will stimulate further research.

We are appreciative of the generous aid received in the preparation of this work. Without this assistance much would be lacking. Frank L. Hess of the United States Bureau of Mines supplied numerous out-of-print papers and a number of valuable photographs. Hugh S. Spence of the Canada Bureau of Mines also gave invaluable assistance with papers, photographs, and personal communications.

George L. Clark at the University of Illinois cooperated

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Acknowledgment is made to the following institutions for photographs and valuable data helpful in preparing this work: United States Bureau of Mines, Carnegie Institution of Washington, National Bureau of Standards, Chesbert Ultraviolet Lamp Company of San Francisco, The Fisher Instrument Company, General Electric Company Laboratories, The Conti-Glo Division of Continental Lithographing Company of Cleveland, Canada Bureau of Mines in Ottawa, Canada, and the Eldorado Mines of Great Bear Lake, Canada.

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I

ATOMIC POWER

Introduction

THE Age of Atoms has just begun. And the beginnings of a new science are arising. The borderline between chemistry and physics is rapidly vanishing. The distinction between chemists and physicists is diminishing. A new group of men serve the new science which actually can be considered fundamental to chemistry and physics, since both are effectively interpreted on its basis. An entire new literature is being formed and the somewhat formidable terminology evolving is evidence of all this. But the applications are much more striking and the promise of fresh utility re-enforces interest and action. The practical aspect has stimulated play in theory. A multitude of fields have benefited by the knowledge in an astonishingly short time. This proves its worth. And this forecasts the value of services to be rendered.

Etymologically, an atom means something which cannot be divided. Generally the term is applied to that chemical individual which has not yet been divided. Now that the atom has been shown to be an extremely complex particle the entity ceases to be an atom. From this it is more correct to say that matter is not composed of atoms but made up of molecules. And molecules, therefore, by definition are made up of atoms.

The realm of chemistry, according to this premise, would be limited only to molecules and actions which occur in systems of molecules. Physics would then be concerned with systems of atoms and the properties of these systems as a whole, not being especially interested in the individual so much as with the entirety. Therefore, chemistry and its

lower limit—the molecule, can be defined, as well as interpreted on the basis of physics and its lower limit—the atom. In both, emphasis is on systems acting more as a whole rather than on their defining units, i.e., atoms or molecules.

But the atom is a system in itself. It is a composite structure resolvable into components of its own. Three components, electrons, protons, and neutrons have been demonstrated by an abundance of experimental evidence although others exist, their placement and actions in the scheme being known to a lesser degree.

The atom, basic to physics and chemistry, consists of a comparatively heavy nucleus surrounded by electrons. The electrons move in their orbits about the central nucleus which is many times their size. Electrons were first discovered in 1898 by J. J. Thomson in his experiments with cathode rays. The work of Thomson showed that the rays behave like streams of minute particles, this being indicated by their action under the influence of a magnetic or electric field.

The classic researches which resulted in the determination of the absolute values for the negative charge electrons were shown to possess, together with the small mass, were those of R. A. Millikan. While the negative charge on electrons was demonstrated by Thomson, it required the more exacting studies by Millikan, some years later, to obtain their exact value from whence the mass of the particle could be calculated. Further, the ratio of the mass of the electron to that of the hydrogen atom was found to be about 1 to 1842 and this observation led to the conclusion that the bulk of the atom is centralized in the nucleus.

Since the atom itself possessed no charge, it inevitably followed that components with equivalent and opposite charges had to be present. The hydrogen ion had been known previously to possess a positive charge equal in magnitude to the electron. This, when correlated with the fact that the hydro-

gen atom is the simplest known, resulted in the assumption that the hydrogen ion is the carrier of positive charges in all atoms. The hydrogen ion, since 1920 called the proton by the physicist, had been known to the chemist for a long time. Although not immediately recognized as such, the work of Goldstein in 1886 resulted in the first description of protons, these being observed in an evacuated vessel during passage of high potential discharges between two electrodes. .

Our knowledge regarding the structure of the atom would not be as highly matured had not the amazing insight of Rutherford been directed toward its problems. As early as 1904, Rutherford predicted the existence of a nuclear atom. Subsequent experimental work confirmed these predictions. For example, the investigations of Geiger and Marsden on the scattering of alpha particles from gold foil. This work consisted of observing the scintillations due to the scattered particles impinging on a zinc sulfide coated screen. These observations led to more definite ideas regarding the dimensions involved in the atom.

At about the same time the classic work on atomic numbers was being performed by Moseley. The fundamental work of Moseley first clearly defined the concept of atomic number. The theoretical studies, constructed about experiments on X-ray spectra, led to arrangement of elements in an orderly fashion in the periodic system and allowed the assigning of an ordinal number to each element. The atomic number expresses the number of electrons in the extranuclear system and denotes the charge equal and opposite to the electronic charge on the nucleus.

Moseley was indeed as extraordinary as his work. A. K. Solomon pointed out that Moseley was so exceptional that every writer who mentions him or his work always makes a point of commenting on the brilliance of the young physicist. The clarity of his insight remains astonishing, even today,

when all the results of his experiments are accepted as a matter of fact. Moseley, when only 27, lost his life in battle action at Gallipoli in the summer of 1915.

Meanwhile radioactivity had been discovered by Becquerel in 1896, shortly after Roentgen had announced the existence of X-rays in 1895. The stupendous influence, that radioactivity was to have on shaping ideas about matter and energy, was already becoming evident. The discovery of radioactivity by Becquerel involved uranium and has since included several other elements. An element which is naturally radioactive constantly breaks down through the release of part of its structure, thus degenerating into an element which is lighter and less complex. The breakdown occurs through the emission of either alpha or beta particles. Oftentimes gamma rays, short wavelength X-rays, accompany radioactive disintegration.

Radioactive substances were often found to be associated with helium, a fact which was soon correlated with the radiations emitted. It was found that the alpha rays given off from radioactive materials were helium ions. This led to the proposal of the disintegration theory of radioactivity by Rutherford and Soddy, another advance in science and another token of Rutherford's insight.

The alpha rays consisting of helium ions were first named by Rutherford. The beta rays, or high speed electrons, whose velocity often approaches the velocity of light, were named by Becquerel. It was due to the emission of beta rays that radioactivity was discovered. Potassium uranyl sulfate is one of the first substances in which this peculiar activity was noted.

The nucleus of the atom, knowledge about which has also been an outgrowth of the influence of radioactivity, is comprised of protons and neutrons. The neutron is another prediction by Rutherford which came true. In 1920 Rutherford

predicted the existence of a chargeless particle of about equal mass to the proton but with properties entirely unlike the two charged particles, i.e., proton and electron, known at the time. Twelve years later, in 1932, Chadwick discovered a nuclear particle of approximately unit mass as a result of a series of experiments on artificial disintegration. Before the discovery of the neutron the nucleus was supposed to be made up of protons and electrons. With the newer data about the neutron, this idea was discarded and replaced by one favoring a nucleus composed of protons and neutrons.

The number of protons and neutrons in the nucleus is equal to its mass number denoted by A . Isotopes, revealed from developments in radioactivity and by other approaches, are the atoms of any one element which are unlike in mass but otherwise practically identical. Elements such as tin may be composed of as many as ten different kinds of atoms, mixed in slightly varying proportions. The chemical atomic weight merely denotes the average values found in determinations on the naturally obtained substances consisting of mixtures of the various isotopes.

The number of protons in the nucleus is equal to the atomic number, denoted by Z . The number of neutrons has been found to be A minus Z , values for which determine the variance in mass of the isotopes for the particular element. Isotopes have been defined as having identical chemical properties but indications are that even this notion may eventually be discarded. Atomic masses, denoted by mass number, are similar to chemical atomic weights, i.e., they are purely relative figures based on comparison. Mass numbers are ascertained from an atomic ion taken as a standard and although not directly deductible in grams can be obtained in such terms by instrumental means.

On the other hand, chemical atomic weights become open to question when it is realized that the standard for compari-

son is oxygen, a naturally occurring mixture of three isotopes. It is apparent, however, that for chemical work this is adequate since all of the isotopic atoms behave in a similar manner and the proportions of the isotopes remain fairly constant. A number of investigations are being conducted which will allow interpretation of chemical atomic weights on the basis of standard elements such as fluorine or iodine which have no isotopes.

It has become customary, although the notations are not entirely standardized, to denote the atomic number of an element along with its mass number and symbol, thus preventing confusion where isotopes act as singular individuals aside from the chemical sense. It follows, therefore, for an isotope of element R, of atomic number Z, and mass number A, the notation employed would be ${}_Z\text{R}^A$. Quite often when little or no importance can be attached to Z it is omitted from the notation or merely assumed. In uranium ${}_{92}\text{U}^{235}$ the ordinary practice is to speak of the isotope as uranium 235.

About 280 natural isotopes are known, an average of about three for each element. However, several elements have nearly a dozen isotopes and a few have only one. Mercury has eleven while uranium has three, the intermediate member of mass 235 being of utmost interest. The two others, 234 and 238 exist in a ratio of about one to 17,000. Artificial isotopes can be prepared which have not been found to occur in nature.

So the term atom at this stage loses a considerable amount of its original meaning and can serve no further, according to the premise, other than allowing approximation of the boundaries of the upper limit to the new science and a lower limit to physics with chemistry being defined in terms of the latter. The term atom as an entity merely gives a relative conception as to the upper magnitude of the systems involved in the new science. It does not convey meaning as to the

variety of components and systems of atomic and subatomic magnitude involved in the new science. The components of atoms, and other particles of subatomic size, as well as energy, enter into atomic reaction forming entities which are not described adequately by the term atom in its original sense.

The molecules which react in chemical processes appear to be endless in number and variety. A few of the many-fold reasons for this are immediately apparent because of their clarity and despite their obscurity. The nature of the chemical bond is a basic factor although its true characteristics are not known with certainty. The mechanisms which involve molecules, i.e., chemical reactions, are further based on valency. Only a few aspects of the problem of valency have been solved. Many others are seemingly remote. Valency in its usual sense is known to the extent that accurate prediction of the actions of many different molecules can be made.

But this does not hold true for a number of chemical elements and the somewhat awry-appearing combining capacities of intermetallic compounds. At this point the chemistry transcends into the physics with the region of uncertainty between them extraordinary by its controversial and thought-provoking nature. The exact point of emergence of chemistry into physics may be somewhat inadequately termed an interstice between physical chemistry and chemical physics.

As contrasted to the molecules in ordinary chemical processes, the particles involved in atomic reactions are comparatively few in type and number. The importance of electrons, protons, and neutrons in the construction of the atom in the ordinary sense has already been pointed out. In the disintegration of matter, referred to as radioactivity, the atoms themselves break down into relatively simpler elements together with the emission of subatomic particles. Natural radioactive disintegration processes are similar.

In the synthesis of atoms, e.g., artificial radioactive elements, atomic reactions involving subatomic particles and radiation allow the creation of entities of atomic magnitude. In short, the process can be considered in many ways the reversal of radioactive processes.

In the synthesis of these new entities which are systems in themselves several reacting components other than electrons, protons, or neutrons, are available for use. Even these are not always single subatomic particles. When in the case of alpha particles which are helium ions, ${}_2\text{He}^4$, they may be entities in themselves. Beta particles, electrons, are of two types depending on their charge. The well-known beta particle is an electron with a negative charge and is the particle which makes up the extranuclear portion of the atom. Electrons with positive charges can be considered as beta particles, being called positrons. They are equal in mass to the ordinary electron, differing only in the sign of their charge.

The isotopes of atoms can be used on occasion in atomic reactions which lead to the synthesis of atomic entities. Deuterons, heavy hydrogen ions, are of this sort. The methods for inducing the components to react depend on the source and energy, as well as the nature of the particle. Many particles are ejected from naturally radioactive materials with large amounts of kinetic energy. On the other hand, instruments can be used to prepare a particle from a natural, or less often from an artificial atom, give it energy, and induce it to react with other nuclei or particles. The cyclotron is illustrative of a machine in which the synthesis of atomic species is accomplished.

In paralleling chemistry, physics, and the new science, it is apparent which is the most fundamental of the three. According to the previous notion, two can be defined almost wholly and interpreted more logically on the basis of the new science. The three fundamental sciences bear a more definite

relationship to each other and in a strict sense their lines of demarcation are somewhat more patent when defined according to the lower limit of the magnitude of entities comprising their systems.

In chemistry the lower limit is the molecule and chemical processes involve systems of molecules. In physics the lower limit is the atom, with atoms being defined as entities and acting in physics more as systems rather than as individuals. In the new science, basic to both, the atom is a system in itself. The lower limit of the new science is defined as consisting of the point at which the annihilation of matter to energy takes place. Then the lower limit of the new science is energy itself.

A positron and an electron can combine with their energies being transformed into the energy of gamma rays. This is referred to as the annihilation of matter. The process actually has been observed by Crane, Thibaud, and others. Positrons can be produced by the atomic reaction between carbon and deuterium. A carbon block is bombarded by neutrons and after proceeding through several intermediate stages, e.g., radioactive nitrogen, positrons are emitted.

In the annihilation of matter two oppositely charged particles combine to form two photons, i.e., energy, of equal magnitude. In the reverse of the process, called materialization of energy, a single photon breaks up into two oppositely charged particles.

Further illustration of the lower limit of the new science is in the formation of pairs of charged particles. It has been shown in cloud chamber experiments that the passage of gamma rays through a heavy element such as lead produces pairs of oppositely charged particles which originate from a common point. The individuals in this pair have been shown to be an electron with a negative charge and a positron with a positive charge.

Additional analogy is interesting. The chemical reactions between systems of molecules often occur in a medium comprised of other systems of molecules, i.e., the solvent. The analogy, then, is to the new science where the atomic reaction occurs in or is associated with energy, i.e., the medium. Just as in chemical reactions the solvent may enter into the reaction. In the new science the interdependence of the reacting particles and their media, i.e., energy, as evidenced by the reaction product is fairly obvious.

Of all the definitions of chemistry or physics effectively suited to interpret chemistry, physics, and the new science on a common basis, perhaps best is that of Paracelsus who, in the middle of the sixteenth century, proposed an impartial answer to the then not too impartial inquiries. He stated "Chemistry is the art of resolving bodies." Then, according to the notion being presented, the Paracelsian definition should be modified to "Chemistry is the art of resolving bodies into molecules." And further, "Physics is the art of resolving bodies into atoms." Then the new science, on these bases should imply "The art of resolving bodies whose lower limits are energy."

The explanation thus far may be considered shallow by tacitly neglecting, although not discounting, energy except in its relationship to the lower limit of the new science. The annihilation of matter and materialization of energy has already been pointed out. However, in lieu of present knowledge it may yet be safe to assume the validity of the laws of conservation of mass and energy but decidedly less safe to conjecture about the origin and source of energy. The relation of radiation with atoms in physics and of reaction energy with molecules in chemistry need not be altered by this explanation in spite of several manifest assumptions.

The new science, basic to both physics and chemistry whose lower limits have been defined, is interpreted through the

methods of chemistry and physics. The products of atomic reactions can and are subjected to the usual, although by necessity somewhat refined reactions used in analytic chemistry. Thus by characterization through reaction products formed with well-known chemical substances, they can be identified. Should the methods of chemistry fail because of the quantities involved the methods of physics can be used. In this the properties of atoms as a whole serve to identify the atomic reaction product. A typical example of characterization of a system of atoms as a whole is in determination of isotopic constitution by the mass-spectrometer.

Also, methods are in use which make possible the identification of a single entity or particle. The techniques used for the identification of single particles may involve the cloud chamber in conjunction with photographic apparatus. The application of fields of energy and the use of metal barriers will allow identification of many of the better known particles. Geiger-Mueller Counters have been constructed which will record the passage of a single alpha particle passing through a liter chamber every hour.

In chemistry the explanation of valence is founded on the extra-nuclear electrons in an atom. In peculiar and lesser known combinations, which occur within the realm of chemistry, such as solvation, auxiliary valency, coordination capacity, dipole moment, inner complexes and intercalation compounds, induced precipitation, solvent similarity in solubility, catalysis, and masking reactions, the electron generally assumes a role of varying importance. Likewise, in physics the arrangement and distribution of electrons can be approached by the study of atomic spectra.

It will be noted that the foregoing explanation has preferred the use of the term *new science*. The intention has been to prevent confusion, or perhaps even bias of interpretation because of outlook through fields such as, natural radio-

activity discovered by Becquerel, artificial radioactivity discovered by the Joliot-Curies, transuranic elements described by Fermi and his co-workers, radiochemistry developed by O. Hahn, and the host of others.

The physicist from his standpoint has called the new science atomic physics, nuclear physics, and sometimes chemical physics. But the chemist from his standpoint, prefers terms such as nuclear chemistry, the chemistry of atomic nuclei, and perhaps even physical chemistry to denote his claims on the new science.

These are all parts of the new science which has not yet matured. And the parts themselves have matured to a widely varying extent. It would be difficult, if not unwise, to assign the new science a definite place in either chemistry or physics although both, especially the latter, may have strong claims on it. To assign the new science definitely to either, may restrict its maturation along independent lines.

Doubtless there is much regarding the new science which yet remains to be discovered. It is desirable that it should be permitted to develop independently along its own lines, employing the methods of chemistry and physics as much as possible, but without restriction which might result from interpretation through chemistry or physics or both.

Atomic Power Possibilities

A great deal is being written and said about the available strategic minerals within the borders of the United States, but seemingly little thought is being devoted to the future possibilities of the uranium minerals. Obviously, if and when, the separation of the uranium isotope 235 can be accomplished on a practical commercial basis, all deposits of uranium minerals will instantly assume tremendous importance.

The sole source of uranium 235 is from uranium minerals,

or from refined uranium salts, which of course originated from minerals. Pitchblende (uraninite) occurs at various localities in the United States, but not in large deposits—a few hundred pounds are mined from time to time. By far the most extensive deposits in the United States are the carnotite beds of Colorado and Utah. Some years ago, prior to the discovery of rich pitchblende ores in other parts of the world, large tonnages of carnotite were mined in the United States, primarily for the radium and vanadium content, the uranium was looked upon as a by-product. The carnotite deposits of the United States, are fortunately of considerable extent, and much of the ore contains 50 per cent or more of uranium oxides.

For some years science has attempted to solve the riddle of the vast energy locked up within the atom, and thus make atomic power or energy available to man. Recent researches have shown that nearly all elements are composed of atoms having different atomic weights. It was thought for many years that all atoms comprising an element had exactly the same atomic weight. For example, for the heaviest of all elements, uranium, the atomic weight was stated to be 238. However, it has been learned that uranium is composed of several isotopes—atoms having different atomic mass. Among the isotopes of uranium, some are present in proportions as low as 1 to 17,000 of 238, the “normal” uranium atom. It is the uranium isotope with the atomic weight of 235 in which we are interested as a potential source of atomic energy. The proportion of uranium 235 present in all uranium minerals and salts of uranium, is 1 to every 139 of uranium 238.

The separation and isolation of uranium 235 is already a laboratory accomplishment, but means are being studied to make commercial production feasible. Locked up within the 238 atoms, isotope 235 is harmless and meek, but once sepa-

rated it is capable of releasing an unbelievable amount of energy and power. Science is attacking the separation problem in a number of ways, including experimentation with twelve or more different types of apparatus by which uranium 235 may finally be separated on a commercial basis.

The atom splitting agency is the neutron, discovered only recently, and itself a part of the hearts of atoms. The bombardment of uranium with neutrons will split its nucleus and release many millions of electron-volts of energy. Otto Hahn was one of the first to experiment with uranium under neutron bombardment. Dr. Liese Meitner, an associate of Hahn, and R. Frisch, suggested the idea of uranium splitting into other elements under this treatment. Although previously unheard of, other workers proved this to be a fact. Atom smashers were brought into service, and early in 1939, this sensation of theoretical physics was confirmed by at least four independent investigators, including Dr. John A. Fleming working with a new atom smasher at the Carnegie Institution of Washington. These first experiments required an expenditure of about 3,000,000,000 electron volts of energy to release 200,000,000 electron volts of energy from a uranium atom.

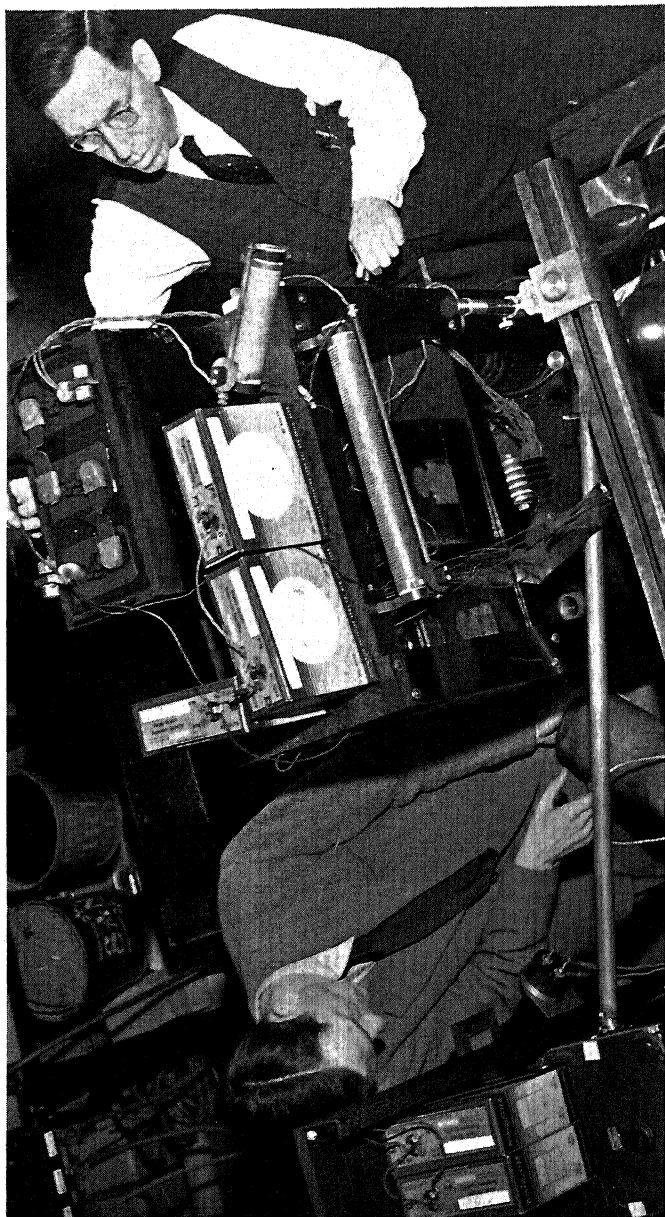
In experiments made in 1939 with an instrument known as a mass-spectrometer, A. O. C. Nier of the University of Minnesota, was the first to isolate a minute amount of uranium 235, and proving conclusively the fission of the uranium atom. At the outset the separation of uranium 235 was a very slow and costly matter, and would require some 75,000 years to separate a single pound of this power producing isotope. However, the separation methods were quickly improved upon. The thermal diffusion apparatus, for example, holds promise of speeding the concentration of uranium 235 by a factor of some 11,000 times. The thermal diffusion tubes are not costly and easy to construct, and it has been

suggested that a whole series may be operated simultaneously for the production of the power isotope.

As a source of atomic power pure uranium 235 may not be required for practical purposes. Dilutions of 235 have been suggested as a means to better control the release of energy. The fourteen foot thermal diffusion apparatus recently constructed in the General Electric Company Research Laboratory may be the forerunner of equipment which may some day separate the power producing uranium atoms in commercial quantities.

Huge, heavy, and costly cyclotrons have often dominated uranium fission experiments in the United States, but equipment of this kind is not necessary to set off the reaction and release atomic energy. For example, a small amount of radium, mixed with beryllium and embedded in a block of paraffin, will suffice as a source of neutrons for the bombardment of uranium, the uranium splitting with its own chain reaction completing the work. Another problem is the control of the power within the uranium atom when released by atom smashing; an explosion might result. It has been shown that uranium 235 will release enormous energy when attacked by a relatively unenergetic neutron. In this atomic reaction more neutrons are produced which are capable of producing more uranium fission. And so it is thought the explosions might continue, just as when dynamite explodes, one atom setting off another. Neutron bombardment of a specimen of pitchblende does not cause an explosion or release of appreciable atomic power, because the uranium 235 atoms are greatly diluted with inert atoms. The attacking neutrons will expend their energy futilely in colliding with unresponsive atoms. Since the explosiveness is caused by slow neutrons of low energy, this may suggest a means of controlling the release of energy for application to practical uses.

If science is ever to create a source of atomic power by the



Dr. H. C. Pollock, left, and Dr. K. H. Kingdon with their mass-spectrometer, General Electric Company Research Laboratory. Dr. Pollock is shown cooling part of equipment with liquid air.

liberation of atomic energy in uranium fission with low energy neutrons, chain reactions will make the fission self-perpetuating. Recently four French scientists have been successful in the development of a chain reaction, although they report that the chain effect is convergent, gradually weakens and ends. However, it is entirely possible that a continuous and non-expiring chain reaction can be developed to function in a successful manner and under due control. The French scientists found that eight neutrons are liberated per primary uranium fission, whereas only 3.5 neutrons per fission had been previously reported. The difference, they believe, is the evidence for the long-sought chain reaction and due to secondary and tertiary reactions in the chain.

The French scientists used a mixture of radium and beryllium as a basic source of neutrons. The neutrons from this source was used to bombard 660 pounds of uranium oxide contained in a large copper sphere, kept immersed in a tank of water. The purpose of the water immersion was to slow the neutrons and aid in the control of the reaction.

Speaking before a meeting of the American Physical Society, late in 1940, R. D. Present of Purdue University, stated that the possibilities of uranium 235 as a source of atomic power may be greater than has hitherto been supposed. According to R. D. Present, it is theoretically possible for the nucleus of the uranium atom to divide into three parts as well as two. Such a reaction would yield slightly more energy than binary fission.

Early in 1940, Herbert L. Anderson of Columbia University described measurements of the resonance capture of neutrons by uranium. This is significant because of the ease with which a neutron can be captured by a uranium atom and determines how readily a splitting of uranium atoms may occur. The studies of Anderson indicated that neutrons having only five electron-volts of energy are involved in the

liberation of energies which, for each nuclear fission, amount to over 150 million electron-volts.

In recent years considerable thought has been given to the problem of our rapidly vanishing reserves of petroleum and coal. In all probability petroleum would be first exhausted, but gasoline could still be obtained from coal by well-known methods. Eventually it would be necessary to utilize the lower grade coal deposits, and these too would finally become depleted. The wars in Europe have been, in part, a struggle for the fossil-stored sunshine and energy of past ages, locked within deposits of oil and coal. Obviously a source of power derived from the energy locked within the atom would solve a problem vital to civilization.

Only a few years ago the probability of the release of atomic power appeared fantastic, but early in 1939 the fission of uranium, with the release of enormous energy was demonstrated in a number of laboratories. According to many investigators in this field, the future hope of releasing commercial amounts of atomic energy appears to be dependent upon improvements in present known methods of nuclear fission. The cyclotron as developed by E. O. Lawrence of the University of California, also justifies the hope that eventually inexpensive and efficient power may be derived by uranium fission.

The amount of research being expended upon the vital problem of atomic power is small compared with the reward of achievement. Many of the present experiments are being conducted in laboratories without any particular commercial objectives in mind. The extreme importance of a source of atomic power would seem to warrant the expenditure of far greater sums in these researches. Recently the Rockefeller Foundation expressed faith in the possibilities of nuclear physics by an award of over one million dollars to be devoted to the construction of a huge new cyclotron for research.

It has also been suggested that use could be made of a few tons of the gold stored at Fort Knox, in the construction of thermal diffusion and centrifugation apparatus, to be used in experimenting with the separation of uranium 235 in the gaseous uranium hexafluoride. The stored gold serves no useful scientific purpose, but would here serve to resist the uranium hexafluoride which is highly corrosive to glass and ordinary metals. Moreover, the gold applied in this work would not involve its loss. The thermal diffusion apparatus for the separation of uranium 235 holds pregnant possibilities.

In addition to the possibilities of atomic power, apparatus like the cyclotron may assume tremendous importance in the creation of various artificial radioactive substances of considerable value in the industries, sciences, and arts. For example, the large cyclotron can comparatively quickly create radiosodium equivalent to huge quantities of radium. True, the artificial product is of short life, yet it can be created in quantity and at will. Moreover, apparatus of this type offers experimental possibilities that will doubtless develop many new and valuable substances at present unknown. The effect of neutron bombardment upon numerous substances is still unknown, but all agree that research will reveal material of considerable practical value aside from the possibilities of atomic power. A new world of scientific knowledge is about to be revealed.

Fantastic as they may appear, let us speculate upon a few of the possibilities of uranium 235 as a source of atomic power. Science has already won its first great objective in its struggle to release the vast energy stored up within the atom. In revealing this secret, science has presented to the human race a great problem and undreamed-of opportunities. Some believe that it will be many years before atomic power will be generally available, and perhaps never. On the other

hand many scientists believe that the realization may come within ten years or much sooner. This latter view seems wholly reasonable. Since work upon the problem was first started only a few years ago there have been numerous improvements, and the production of isotopes speeded up thousands of times.

Probably no one can say with accuracy when the dream of science will be fully realized. Who could venture to predict the future possibilities of the radio, when Marconi first announced wireless telegraphy a few decades ago? In view of the past achievements of science, it is probably safe to predict that some day atomic power will be an actuality. It may require many years to reach the final goal. On the other hand some worker may solve the riddle tomorrow. The way has been cleared on experimental and theoretical grounds, and the course now lies open for improvement in fission technic, as well as separation of the isotopes.

Fortunately a means has already been found to control the atomic disintegration of uranium 235. The presence of the uranium isotope 238 acts as a slowing down agent, and these properties may prove valuable in the practical control of atomic energy processes. Moreover, the high speed neutrons shot forth from uranium 235 may also be controlled by water. It is fortunate that the energy release process requires slow neutrons and that the hydrogen atoms in water offer an excellent means for control. Hydrogen atoms and neutrons have about the same mass, hence it is possible for high speed neutrons from uranium 235 to transmit the greatest amount of their energy to the hydrogen atoms when they meet in collision. This immediately suggests the use of uranium 235 as a means of quickly heating water.

Probably if uranium 235 is used as an atomic power source the energy will be removed in the form of heat. The slow neutrons acting upon uranium 235 would cause the entire

mass to become incandescent, and the water in contact with it for control purposes could be drawn off in the form of steam for power. In short, the uranium would act in the same manner as coal under a boiler. The fact that uranium 235 is disintegrated by slow neutrons is fortunate, otherwise if the process would continue at the rate at which it starts, the whole mass being quickly converted into energy, a violent explosion might result. Water in the form of steam will not slow down the neutrons, hence with no slow neutrons present to act as activators the disintegration of uranium 235 would be suspended until more water was added.

Under controlled conditions it has been estimated that one pound of uranium 235 would provide as much energy and power as about 5,000,000 pounds of coal. The transport unit of the future would require only a single charge of fuel, a few pounds at the most, to enable operation for the life of the machinery. If a dwelling house required twenty tons of coal per year, only one gram of uranium 235 would be required to heat the dwelling in the winter, cool it in the summer, for a period of over 200 years. Under these conditions the smoke nuisance of the great cities would be eliminated. The auto engine would probably be changed from internal-combustion to steam, with the elimination of certain gears.

For various reasons pure metallic uranium 235 would probably not be found practical as a source of atomic power. A mixture of the isotopes 235 and 238 would doubtless offer a more readily controllable means for power purposes. For example, if a mass of pure uranium 235 were dropped into water, the water would slow down the neutrons and the atoms would start fission in a chain reaction. The uranium would promptly become incandescent and change the surrounding water into steam with explosive violence.

As an explosive, uranium 235 offers some fantastic possibilities. The total-energy content of atoms, weight for

weight, is said to be some eighteen billion times greater than the energy yielded by any known chemical combustion process. When a uranium 235 nucleus explodes it releases about 200 million electron volts. When a molecule of T.N.T. explodes it releases only five electron volts. Pound for pound an "atomic" explosion would be millions of times more powerful and destructive than any explosive known at present. For peaceful pursuits of man, explosives are invaluable. We will not contemplate the appalling possibilities of "atomic gunpowder" in warfare. Obviously the nation which achieves the goal of atomic energy, and holds the secret, could promptly rule the world if it so elected.

There is another possibility which may be forthcoming from experiments with apparatus used for atom splitting; the beneficial effects of neutrons in treating cancerous growths in the human body. Streams of neutrons may offer a more satisfactory means of treating deep seated cancerous growths than X-rays. Artificial radioactive substances of considerable potency can be produced in apparatus like the cyclotron, and these may prove of great value in medicine. The artificial radioactive substances will also find value for research in the transmutation of elements, and doubtless for numerous other practical purposes.

The development of atomic power would have a profound effect upon our civilization, and would open up many new roads to human happiness and comfort. The discovery of laboratory methods for the separation of uranium 235 holds promise for the dawn of a new era for science and civilization. What role uranium may play in contributing to the advancement of man is a matter of conjecture but filled with a world of possibilities.

THE URANIUM MINERALS

URANIUM has been found in commercial quantities in the United States in two minerals, carnotite and pitchblende. As a source of uranium in the United States, carnotite is by far the most important ore. Uranium is the mother of radium, hence all uranium minerals and salts contain recoverable radium.

The United States Bureau of Mines classifies the uranium ores as of three general types: (1) the uraninites, (2) the columbium-titanium tantalates of the rare earths and uranium, and (3) the secondary uranium minerals.

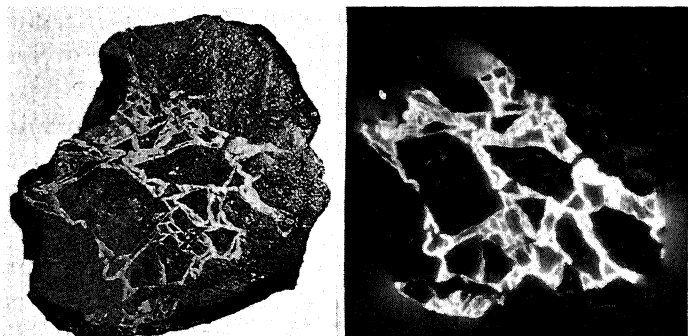
Type 1. The uraninites, which are the richest in uranium, include crystalline varieties such as broggerite, cleveite, and nivenite. These varieties occur in pegmatites and often in well-developed crystals. Pitchblendes are amorphous uraninites occurring often in metalliferous veins and associated with various sulfides, including silver, iron, lead, cobalt, zinc and other metals. The terms "uraninite" and "pitchblende" are often used synonymously, but the latter term is generally applied only to the amorphous and impure forms of the mineral.

Pitchblende often occurs with botryoidal surfaces and a characteristic conchoidal fracture. It is black or grayish-black in color, often with a glossy or pitch-like luster. The pitchblende of Great Bear Lake, Canada, has a brownish-black color on the freshly broken surface. The hardness of pitchblende is approximately that of steel (5.5), while the specific gravity varies with the purity and ranges from about 5 to 9.7.

Type 2. The uranium minerals of this group are of com-

plex chemical composition, often well crystallized, occur in pegmatite dikes, and generally have a specific gravity over 4. They are generally dark brown or black in color.

Type 3. The secondary uranium minerals are all derived from the alteration or decomposition of primary uranium minerals, and may occur in both igneous and sedimentary formations. The various secondary minerals include phos-



Polished section (left) of pitchblende ore, El Dorado Mine, Great Bear Lake, Canada. Light colored lines are veins of pitchblende forming a network around brecciated fragments of rock. Radiograph (right) showing the association in greater contrast. (Photo: Canada Bureau Mines)

phates, carbonates, arsenates, sulphates, silicates, vanadates, and uranates of uranium. Most of them are characterized by bright colors. Being formed relatively recently many of the secondary minerals have not yet reached an equilibrium as denoted by the uranium-radium ratio. Carnotite, autunite, and torbernite are typical of this group.

Pitchblende

Pitchblende (uraninite) is a complex oxide of uranium with variable amounts of lead, iron, copper, bismuth, and the rare elements radium, thorium, yttrium, helium, and argon. Radium was first discovered in and isolated from pitchblende.

Uraninite crystallizes in the isometric system, but crystals are rare, the mineral usually occurs massive or botryoidal. Depending upon the purity the percentage of uranium oxides in pitchblende varies from about 64 to 89 per cent.

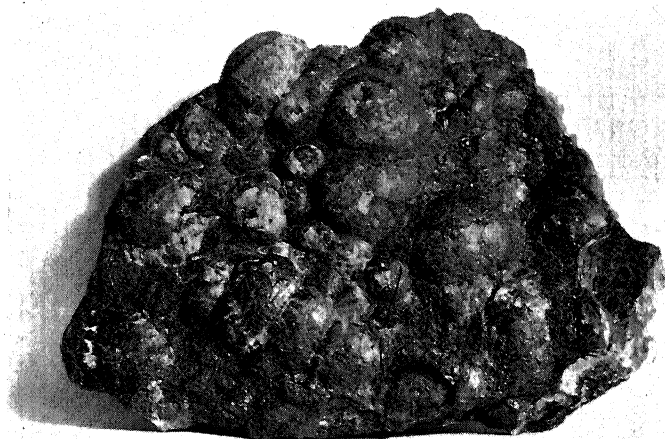
From a physical point of view pitchblende is an extraordinary mineral. In it helium was first discovered. The radioactive elements, uranium, radium, polonium, and actinium were also first discovered in pitchblende. The discovery and isolation of uranium and radium in turn led to many important discoveries and advances in chemistry and physics. The scientific conception of the atom has greatly changed since the discovery and study of these radioactive elements took place. Pitchblende is variable in composition, hence several modifications of it have been given variety names including cleveite, nasturan, nivenite, and broeggerite.

The known deposits of pitchblende, sufficiently rich and extensive enough to be considered commercial, are relatively few, and include those of Great Bear Lake, Canada, Belgian Congo, West Africa; the ¹⁹²Joachimsthal district of Czechoslovakia, and scattered deposits of lesser importance in other parts of the world. According to Hugh S. Spence, the Great Bear Lake pitchblende is the richest known considered as tonnage grade of ore. The Great Bear Lake deposits are also thought to be the most extensive known.

The Great Bear Lake deposits at La Bine Point were discovered in 1930, and immediately attracted world wide attention. Developments came rapidly and within a few years some of the properties were in commercial production. By 1939, the Eldorado mine, the chief producer in the region, was stated to yield radium, uranium, silver and other refined mineral products valued at \$300,000 monthly.

The Joachimsthal pitchblende ores were mined extensively prior to the discovery of the richer deposits in the Belgian Congo, and Great Bear Lake, Canada. At Joachimsthal the

pitchblende is associated with nickel and cobalt-bearing veins. Limited amounts of pitchblende occur in many mines of the Cornwall, England, region, in association with nickel-cobalt veins. Uraninite and uranium minerals are found in the pegmatites of southern Norway, but have never assumed commercial significance. Pitchblende is found associated



Botryoidal type of pitchblende, 1400 foot level, number 2 vein, El Dorado Mine, Great Bear Lake, Canada. (Photo: Canada Bureau Mines)

with tin and tungsten minerals in the granites of northern Portugal. Various localities in Russia and Siberia produce limited amounts of pitchblende.

Pitchblende and a formidable series of uranium bearing minerals occur in the granitic rocks of central Madagascar, but the deposits do not appear to have been fully explored or exploited, despite the fact that they have been known for over thirty years. The uranium minerals from the pegmatites of Madagascar include a number of species not known to occur elsewhere.

Pitchblende has been found at various localities in the

United States, but seldom in quantities greater than a few hundred pounds at one time. Several mines in Gilpin County, Utah where pitchblende veins up to eight inches in thickness were encountered, have rated temporarily as commercial producers. The Pegmatite dikes of North Carolina produce small amounts of pitchblende, usually encountered while quarrying or mining other minerals. In mining feldspar near Penland, North Carolina a few hundred pounds of pitchblende are recovered at intervals. Several quarries and mines in Mitchell County, North Carolina also produce pitchblende. Much of the original pitchblende in the pegmatites of North Carolina has been altered to various secondary uraninites.

The extensive pegmatite dikes of the New England states yield small isolated quantities of pitchblende. Pitchblende in acicular crystals has been reported from the Rathgeb mine, near San Andres, Calaveras County, California. Wyoming, Colorado, Nevada and other states have reported isolated occurrences of pitchblende. The nivenite variety of uraninite was mined at Barringer Hill, Llano County, Texas, a locality now inaccessible.

Carnotite

Carnotite is an amorphous, soft, powdery mineral, sometimes talcose or waxy in character. The color is generally a characteristic bright canary yellow, but it may be discolored by iron oxides, organic matter, or other substances. Carnotite is essentially a hydrous potassium-uranium vanadate, having a hardness of from 2 to 2.5, and a specific gravity of from 3.5 to 3.9.

Although uranium and vanadium are chemically unlike, they occur together in carnotite, and both are generally recovered in the treatment of the ore. Vanadium is a member of the phosphorus group of elements, while uranium is more

akin to tungsten and molybdenum. Vanadium is more common to the ferromagnesian rocks, while primary uranium minerals occur in granites and pegmatites; the secondary uraninites, like carnotite, may occur in both granitic rocks and sedimentary formations. Carnotite was first described by C. Friedel and E. Cumenge in 1899. It is widely distributed in the sandstones of the plateau region of southwestern Colorado and southeastern Utah, where it occurs as an impregnation, filling interstices between grains of sandstone, and in cracks and crevices; also in rich masses. Typical analysis of carnotite from Montrose County, Colorado shows the presence of 54 per cent of uranium oxide, and an average of 18 per cent vanadium oxide. Carnotite rarely occurs without the association of other uranium and vanadium minerals.

With few exceptions the carnotite deposits in the plateau regions of Colorado and Utah are in a sandstone of the Mc Elmo age (probably upper Jurassic). Around the uraniferous sandstones is usually an irregular envelope of vanadium bearing sandstone of gray to black color. Like the carnotite, the vanadium minerals are secondary and have been water-transported. In the San Rafael Swell of Utah, carnotite occurs associated principally with the fossil remains of plants. It has been suggested that the organic matter of the plants may have acted as precipitants of vanadium. H. S. Gale noted the association of carnotite with fossil wood, during early investigations.

The origin of the carnotite deposits of Colorado and Utah has been a matter of speculation. It appears certain that the bodies of carnotite were formed subsequent to the deposition of the sandstones in which they occur. Field evidence also points to the conclusion that the carnotite could not have resulted from alteration, in place, of other uranium minerals originally contained in the sands. The shape and position of

the deposits indicates clearly that the uranium and vanadium minerals contained in the sandstones had been transported to their present place. Some of the rich areas of carnotite represent areas of concentration from material already disseminated in the sandstones. It is quite possible that the great carnotite deposits of Colorado and Utah were derived from extensive primary uraninite deposits in granitic rocks of which there remains no trace. As an analogous instance, attention may be called to the deposits of schroeckeringite (dakeite) in gypsum, north of Wamsutter, Wyoming. Unquestionably, the dakeite, a secondary uraninite, was derived from the alteration of uraninite from the adjacent granitic rocks and water transported to its present position in sedimentary deposits.

According to Hoyt S. Gale, who investigated the carnotite deposits in Rio Blanco County, Colorado, the uraniferous sandstones are of Jurassic age. The rock in which the carnotite occurs is a coarse light colored sandstone, exceedingly massive and of considerable thickness. The massive carnotite-bearing sandstone ledges are more resistant to erosion than any of the adjacent formations either above or below, hence the uraniferous sandstones commonly form ridges or hogbacks.

The carnotite deposits on the east side of San Rafael Swell, near Green River, Utah, are of specific interest through their association with fossil plants and wood. According to Frank L. Hess, who studied these deposits in 1911, the uraniferous sandstones of the San Rafael Swell are of Jurassic age. Most of the deposits are situated on the ridge overlooking the valley. All the carnotite is found in a coarse, loosely consolidated, crossbedded sandstone, which in places is finely conglomeric. Much of the sandstone has been cemented by calcite, and petrified wood is conspicuous. Some of the petrified wood is in logs up to three feet in di-

ameter, and often heavily impregnated with carnotite. The petrified wood and plant life occurs largely along one horizon in the sandstone, with the carnotite closely associated. Fossil bone in minor quantities is also associated with the carnotite.

Some comparatively large deposits in the plateau region of Colorado and Utah, carry vanadium with only traces of uranium, but invariably the commercial occurrences of carnotite are vanadiferous. According to Frank L. Hess, the vanadium may occur without visible vegetal fossils, but the carnotite is generally associated with carbonaceous material, either fossiliferous or petroliferous. In the plateau deposits of southwestern Colorado, rich deposits of carnotite have been mined from fossil wood. In the San Miguel River district, two large petrified logs were mined in 1920 for their uranium, radium and vanadium content, yielding 105 tons of ore containing 1.75 grams of radium, then worth \$175,000; uranium oxide worth \$27,000, and vanadium worth \$28,000; a total gross value of \$230,000.

Carnotite is radioactive and contains an average of 3.4 parts of radium in 10,000,000 parts of uranium. An analysis of Colorado carnotite by E. Gleditsch shows 0.0000038 gram of radium per 100 grams of carnotite carrying 16 per cent uranium. A ton of pure uranium would carry 213 milligrams (3.28 grains) of radium.

Carnotite is found at a number of localities in the world and in the United States outside of Colorado and Utah, but the latter deposits are the only ones which have been exploited in a commercial manner. Prior to the discovery of rich uranium ores elsewhere, the Colorado-Utah deposits were mined extensively primarily for their radium content. In 1913 Colorado and Utah produced about 2,700 tons of carnotite ore, with a value of over \$1,000,000 in radium. Over 4,000 tons of ore were produced in 1914.

Production of carnotite in Colorado and Utah dropped during World War I, and practically ceased when competitive production of rich primary uranium ores came in from the mines of Katanga, Belgian Congo. Later with the discovery of the Great Bear Lake, Canada pitchblende deposits, the radium and uranium market was dominated by these two producing regions. The carnotite deposits of Colorado and Utah are of considerable extent, and with reserves that would probably supply domestic needs for uranium and radium for many years to come, should the need arise for their development and exploitation.

Descriptions and occurrences of the lesser important uranium bearing minerals follows. It will be noted that the species status of some is open to question, while pertinent data is lacking on others. Some are essentially identical chemically but differ in optical characteristics, others are varieties of well-known species.

Alpha-hyblite—a white, hydrous basic sulfo-silicate of thorium and uranium. Beta-hyblite differs only in color and optical properties. Both are alteration products of thorite.

Alpha-uranopilite—a lower hydrate of uranopilite.

Alpha-uranotil—hydrated silicate of calcium and uranium, yellow-green in color and occurs in small crystals.

Allanite from Barringer Hill, Llano County, Texas, contains less than one per cent uranium oxides.

Ampangabeite from Madagascar contains from 12 to 19 per cent uranium oxides. A columbate of uranium, rich in iron, and containing titanium and tantalum.

Anthraxolite, a carbon mineral from near Port Arthur, Ontario, is slightly radioactive due to traces of uranium oxides.

Autunite is one of the most widely distributed and one of the most important of the secondary uraninite minerals. It

is frequently associated with pitchblende and forms coatings and fills crevices on pitchblende and the adjoining rocks. It is commonly noted in the pitchblende bearing pegmatites throughout the world. Autunite is a phosphate of uranium and calcium, containing from 55 to 62 per cent uranium oxides, and may be distinguished by its characteristic yellowish-green color, and powerful yellow-green fluorescence un-



Near view of one of the dumps of the Club Camp workings in Heiroylyphic Canyon, lower San Miguel River, Montrose County, Colorado. The workings produce uranium and vanadium minerals. (Photo: A. D. Riley)

der ultraviolet radiations. When some of the calcium in autunite is replaced by barite the mineral becomes uranocircite.

Becquerelite, a hydrated uranium oxide, occurs in the uranium ores of the Belgian Congo, contains 86.51 per cent uranium oxide.

Bassetite, close in composition to autunite, occurs with

other uranium minerals in the Cornwall, England district.

Betafite, containing approximately 27 per cent uranium oxides, is a columbo-titanate of uranium with various bases. A. Lacroix in describing the betafite group of uranium minerals from Madagascar includes betafite with samiresite and blomstrandite. Some betafite crystals found in Madagascar weigh several pounds, and one group of crystals is reported weighing over 200 pounds.

Beta-uranotil at the Jachymov mines contains 66 per cent uranium oxides, and usually found as coatings on uraninite.

Blomstrandite from Madagascar contains approximately 20 per cent uranium oxides, with tantalum, columbium, calcium, and rare earths.

Brannerite occurs as small water worn pebbles in the alluvials at Stanley Basin, Idaho. The pebbles are characterized by their black color and high specific gravity, ranging from 4.5 to 5.4. The average uranium oxide content is 43 per cent.

Broggerite is generally considered as a variety of pitchblende. The Ånneröd, Norway, material carries from 76 to 79 per cent uranium oxides, with 6 per cent thorium oxide.

Calciosamaraskite, a calcium-rich variety of samarskite, occurs in the Woodcock mine, Hastings County, Ontario in large masses weighing up to 100 pounds or more. At Parry Sound, Ontario it is found with uraninite. The content of uranium oxides varies from 10 to 13 per cent.

Chalcolite—see torbernite.

Chlopinite, a black hydrated columbo-titanate of uranium and rare earth elements.

Clarkeite, a sodium, lead, uranium oxide, is an hydrothermal alteration product of pitchblende. Analyzed samples from Spruce Pine, North Carolina show 81 per cent uranium oxides.

Cleveite is generally considered as a variety of pitchblende,

rich in thorium and helium. The Arnedal, Norway cleveite contains 76 per cent uranium oxides.

Chinkolobwite is a variety of gummite.

Curite, a hydrous lead uranate, containing a maximum of 73 per cent uranium oxides occurs with pitchblende ores in the Belgian Congo deposits.

Dakeite, see schroeckeringite.

Davidite of south Australia is a complex chromio-vanadate of uranium.

Delorenzite, first described from Piedmont, Italy, is a titanate of iron, yttrium, and uranium, of uncertain composition, carrying an average of 9 per cent uranium oxide.

Dewindtite from Belgian Congo is a canary-yellow hydrous phosphate of uranium and lead, with 55 per cent uranium oxides.

Djalmaite, a tantalate of uranium and other bases, with a small percentage of titanium, is closely related to betafite and samiresite. *Djalmaite* from Minas Gerais, Brazil carries 11 per cent uranium oxides.

Droogmansite, from Belgian Congo has been described as "presumably uraniferous."

Dumontite from Belgian Congo is a hydrous phosphate of uranium and lead.

Eliasite, a variety of gummite, contains 61 to 67 per cent uranium oxides.

Ellsworthite, chiefly a hydrous titanocolumbate, from Hybla, Ontario, Canada, carries 22 per cent uranium oxides.

Enalite, described as a new variety of uranothorite, is hydrous silicate of thorium and uranium, from the Ena district, Japan.

Eschynite (aeschynite), a complex cerium, titanium, and thorium oxide, from the Ural Mountains, contains less than 1 per cent uranium oxide.

Euxenite is best known from Madagascar, where it occurs

in quantities large enough to be considered commercial. It has also been reported from North Carolina. Contains from 4 to 16 per cent uranium oxides together with various rare earth elements.

Ferganite (ferghanite), a hydrous uranium vanadate, occurs in the province of Fergana, Russian Turkestan.

Fergusonite contains from 1 to 8 per cent uranium oxides, together with various rare earth elements. Occurs at various localities in the United States, and was found in considerable quantity at Barringer Hill, Texas.

Fourmarierite, a hydrous lead uranate, from Belgian Congo, is characterized by its dark orange-red color.

Gilpinite, a canary-yellow, hydrous sulfate and uranate of copper, iron, and sodium, was first described from Gilpin County, Colorado. It is identical with johannite.

Gummite, an alteration product of pitchblende, is frequently seen as coatings on pitchblende, and is of doubtful composition. Gummite from Spruce Pine, North Carolina, contains 78 per cent uranium oxides.

Hatchettolite, a tantalum-columbate of uranium, near pyrochlore, occurs with samarskite, at the mica mines of Mitchell County, North Carolina. It carries from 14 to 16 per cent uranium oxide.

Hornbergite is an arsenate of uranium.

Hyblite, a basic hydrous sulfo-silicate of thorium and uranium, is an alteration product of thorite, described from Hybla, Ontario, Canada.

Ianthinite, believed to be a hydrous uranium dioxide, occurs with other uranium mineral in Belgian Congo.

Ishikawaite, a tantalum-niobate of uranium, with rare earths, from Ishikawa, Japan, is close to samarskite in composition.

Johannite, a hydrous sulfate of uranium and copper, occurs with other uranium minerals at Middletown, Connecticut.

cut and elsewhere. It is identical with Gilpinite and contains 67 per cent uranium oxides.

Kasolite, a hydrous silicate of lead and uranium, occurs at Kasola, Belgian Congo, and contains 49.28 per cent uranium oxides.

Kochelite from Silesia contains less than 1 per cent uranium oxide.

Kolm, a variety of bitumen coal, may be uraniferous. The ash of Swedish kolm contains about 3 per cent uranium oxide. An anthracitic mineral from a pegmatite in the Saguenay district, Canada contains 2.56 per cent uranium oxide, equivalent to 35.43 per cent in the ash. The significance of these and similar occurrences remains to be determined.

Liebigite, a uranium carbonate with 38 per cent uranium oxide.

Lyndochite, essentially a thorium-calcium euxenite, contains less than one per cent uranium oxide, first described from Lyndoch Township, Ontario, Canada.

Mackintoshite contains 22 per cent uranium oxide, and is a silicate of uranium, thorium, and cerium. Was first described from Barringer Hill, Llano County, Texas.

Maitlandite, a hydrous silicate of lead, calcium, thorium, and uranium, differs from mackintoshite, in containing some lead and calcium. Occurs at Wodgina, Western Australia.

Medjidite is a variety of uranocalcite.

Mendelyevite, from Lake Baikal, Siberia, contains 23.5 per cent uranium oxide, and is a calcium urano-titanocolumbate. It is referred to the betafite group.

Meta-torbernite, an emerald-green hydrous phosphate of copper and uranium, is found associated with pitchblende in Mitchell County, North Carolina, and with carnotite at Temple Mountain, Utah. F. Rinne showed that heating torber-

nite to slightly below boiling temperature resulted in the loss of 6.86 per cent water, forming meta-torbernite, accompanied by crystallographic changes. The reaction does not appear to be reversible. Meta-torbernite I and meta-torbernite II, are both dehydration products of torbernite formed at different temperatures.

Metazeunerite a green copper uranyl arsenate occurs in the mines of Cornwall, England with other uranium minerals.

Naegite from Naegi, Mino, Japan is apparently zircon with yttrium, columbium-tantalum, thorium, and uranium oxides. It is regarded as a solid solution of these oxides.

Nicolayite a yellow hydrous silicate of lead, calcium, thorium, and uranium, differs from Maitlandite in the state of oxidation of the uranium. Formerly called thorogummite.

Nivenite is a variety of uraninite, characterized by containing about 10 per cent of the yttrium earths and rich in helium gas. The nivenite of Barringer Hill, Texas has a specific gravity of about 8, and contains 65 per cent uranium oxides.

Nohlite, a hydrated variety of samarskite contains 14 per cent uranium oxides.

Orangite see thorite.

Parsonite of Belgian Congo is a hydrous phosphate of uranium and lead.

Phosphuranylite from Mitchell County, North Carolina occurs as a pulverulent incrustation, is lemon yellow in color and contains 27 per cent uranium oxide. It is a phosphate of uranium.

Pilbarite, an alteration product of mackintoshite, occurs as pebbles in the Pilbara gold field, Western Australia. It is described as a hydrous silicate of uranium, lead, and thorium.

Plumboniobite from Morogoro, East Africa is a columbate of yttrium, uranium, lead, iron, and other metals.

Polycrase, a columbate of rare earths and uranium, like euxenite, and occurs in the alluvials of Henderson County, North Carolina, and also near Marietta, South Carolina. It may contain up to 20 per cent uranium oxide.

Priorite, similar in composition to euxenite, is isomorphous with blomstrandine. Originally described from Hitte, Norway.

Randite, a calcium uranyl carbonate, canary yellow in color contains 31 per cent uranium oxides.

Rauvite, a hydrous vanadate of calcium and uranium, is associated with carnotite at Temple Mountain, Emery County, Utah. The average uranium oxide content is 20 per cent.

Renardite the hydrous phosphate of uranium and lead occurs in the Belgian Congo uranium deposits.

Risorite is probably a titaniferous variety of fergusonite, occurring at Risor, Norway, and contains about one per cent uranium oxide.

Rutherfordine, an ocher resulting from the alteration of uraninite, occurs in the Uruguru Mountains of East Africa. It is a uranyl carbonate, containing about 69 per cent uranium oxide. It is not to be confused with rutherfordite which is also a carbonate.

Saleite is a magnesium analog of autunite, associated with other uranium minerals of the Belgian Congo.

Samarskite is rather abundant in the United States, and is sometimes found in large masses at the mica mines in Mitchell County, North Carolina. Large crystals were found in the Fridlund mine near Petaca, New Mexico and described by Frank L. Hess in 1930. The samarskite of Petaca occurs in a pegmatite dike and was shown to be composed of two parts, an older part about 300 million years old, and a

younger part which had replaced the older mineral was about 150 million years old. It contains from 10 to 15 per cent uranium oxide.

Samiresite, a variety of betafite, and a titano-columbate of uranium, lead, etc., from Samiresy Hill, Madagascar contains about 21 per cent uranium oxide.

Schroëckerite (identical with dakeite) was first described from Bohemia in 1873 by A. Schrauf. The "schroëckerite" from Mitchell County, North Carolina, and Bedford, New York, was shown by R. Novacek (1939) to be identical with beta-uranotile. A large deposit of schroëckerite was discovered in 1936, in gypsite, in the Red Desert, about 40 miles north of Wamsutter, Wyoming. It is a hydrated uranium carbonate, with 32.4 per cent uranium oxide.

Schoepite is probably identical with becquerelite, and was first described as a uranium carbonate from Belgian Congo in 1923 by T. L. Walker. It is an alteration product of uraninite.

Sipylite a columbate of erbium, with cerium metals, is near fergusonite in form. Occurs with allanite in Amherst County, Virginia.

Skłodowskite from Belgian Congo, is a hydrous silicate of uranium and magnesium. Isomorphous with uranophane. Some magnesium may be replaced with copper to form cupro-skłodowskite.

Soddyite (soddite) from Belgian Congo, is a yellow hydrous silicate of uranium, with 85.33 per cent uranium oxide.

Stasite is dimorphous with dewindite. It is a hydrous phosphate of uranium and lead, from Katanga, Belgian Congo.

Thorianite is an isomorphous mixture of thorium oxide and uranium oxide in variable proportions, with small

amounts of other elements. The thorianite of Andolobe, Madagascar contains 4.74 per cent uranium oxide.

Thorite (orangite) a silicate of thorium with uranium. Madagascar thorite contains 7 per cent uranium oxide.

Thucholite, a carbonaceous mineral, associated with uraninite in the Pied Des Monts mine, Charlevoix County, Quebec, and described by Hugh S. Spence, was shown to contain 35.4 per cent uranium oxide in the ash. Analysis of Parry Sound, Ontario, thucholite ash gave only 5.8 per cent uranium oxide.

Toddite was described in 1926, from the Sudbury district, Ontario, Canada, by H. V. Ellsworth, as a new uranium mineral, carrying 11 per cent uranium oxides. The mineral may be considered as columbite in which some manganese and iron is replaced by uranium.

Torbernite, a hydrous phosphate of uranium and copper, carrying 56 to 60 per cent uranium oxides, often replaces crystals of autunite. It is identical with chalcolite. Upon loss of water torbernite passes into meta-torbernite.

Troegerite (trogerite) a lemon-yellow hydrated uranyl arsenate, occurs at Schneeberg, Saxony.

Thorogummite, an alteration product, occurs with fergusonite and other uranium minerals at Barringer Hill, Llano County, Texas.

Tyrite, see fergusonite.

Tyuyamunite, a calcium carnotite, is often associated with the carnotite ores of Colorado. First found in Siberia, and described by C. Friedel (1899), as a carnotite having the potassium replaced by calcium.

Ulrichite, a uranium dioxide, occurs in the pegmatites of Branchville, Connecticut. It has been suggested that the original isometric substance of pitchblende is ulrichite.

Uraconite, an uncertain uranium sulphate, containing from 66 to 71 per cent uranium oxides occurs in the ores at Joachimsthal, Bohemia.

Uranium-galena from Bedford, New York, is galena containing uranium-lead isotope of lead 206.

Uranochalcite is a doubtful species.

Uranocircite is derived from autunite by the replacement of part of the calcium in autunite by barium. Contains approximately 47 per cent uranium oxides.

Uranolepidite a hydrous copper uranate, from the Belgian Congo, is identical with vandenbrandeite.

Uranniobite from Norway, is generally considered as a variety of uraninite.

Uranophane (uranotil) a hydrated calcium uranyl silicate, contains from 53 to 67 per cent uranium oxides. Analysis of uranophane from Lusk, Wyoming gave 67 per cent uranium oxides after deducting for impurities.

Uranopilite containing 77 per cent uranium oxides, occurs with uranium minerals in Colorado and elsewhere. Beta-uranopilite is an alteration product.

Uranospathite, previously regarded as autunite, is probably a hydrated uranyl phosphate.

Uranospherite (uranosphaerite) a hydrated bismuth uranium oxide, containing about 50 per cent uranium oxides, occurs with the uranium ores of Schneeberg, Saxony.

Uranospinite, a calcium uranyl arsenate, contains 49 per cent uranium oxides.

Uranothallite, containing from 31 to 32 per cent uranium oxide, occurs on uraninite at Joachimsthal, Bohemia.

Uranothorite, a high uranium and calcium thorite, occurs in crystals in the Mac Donald mine at Hybla, Ontario, Canada. It is associated with thorite and averages 17 per cent uranium oxides, with 46 per cent thorium oxide.

Uvanite a hydrous uranium vanadate is found associated with carnotite in Colorado and Utah.

Voglite, a hydrated calcium copper uranium carbonate, contains 35 per cent uranium oxide, and occurs as coatings on uraninite.

Walpurgite a bismuth uranyl arsenate contains 16.5 per cent uranium oxide.

Wiikite from Impilaks, Finland, is an isomorphous mixture of alpha-wiikite and beta-wiikite.

Yttrialite a silicate of thorium and yttrium metals, and containing about one per cent uranium oxide, occurs associated with gadolinite at Barringer Hill, Llano County, Texas.

Yttrocrasite a hydrous titanate of yttrium earths, thorium and uranium was first described from Burnet County, Texas.

Yttrogummite containing 20 per cent uranium oxide, occurs with cleveite as a decomposition product.

Zeunerite, a hydrated copper uranyl arsenate, contains 56 per cent uranium oxides. It is sometimes found associated with carnotite.

Zippeite a hydrated uranium sulphate, averaging 68 per cent uranium oxides, occurs as coatings on pitchblende ores at Great Bear Lake, Canada. Curiously enough the zippeite at Great Bear Lake does not appear on the ores within the mine workings, but develops on the ore dumps outside the mine. Zippeite occurs with Carnotite in Colorado, and as a powder with gypsite near Fruita, Utah.

3

PROSPECTING FOR URANIUM MINERALS

ABOUT 115 minerals carrying uranium have been described in mineralogical literature. From a commercial standpoint only a few of these are important, since the major portion of the world supply of uranium is, and has been, derived from uraninite (pitchblende) and carnotite. The most important uranium mineral is pitchblende, also the principal commercial source of radium. Uranium ores are comparatively rare, and when primary, like pitchblende they are invariably associated with granitic rocks. The secondary uranium minerals, like carnotite, are derived from the weathering of primary ores, and may be found associated with granitic rocks, or they may be water transported to sedimentary formations. Hence in prospecting for ores of uranium, the granitic rocks and granite pegmatities offer the best possibilities. Aside from the carnotite deposits of Colorado and Utah, which are an important exception to the general rule, the world's most notable and valuable uranium ores are found with granitic rocks.

There are a number of means which may be utilized in prospecting for uranium minerals, these include the use of portable ultraviolet light units, and field instruments like the electroscope, and the Geiger-Mueller counter. The last two instruments operate on the principle of detecting radiations from the radium present in all uranium minerals.

Various types of portable ultraviolet light units are available which may be taken in the field and operated from batteries. Search is made at night for outcroppings of fluorescent secondary uranium minerals, which may be indicative

of commercial bodies of uranium minerals. The fluorescent effect would not be observable during daylight. It has been a rather widespread fallacy that all pitchblende, radium, and uranium ores are fluorescent. Pitchblende and all other primary uranium minerals are never fluorescent, but many of the secondary uranium minerals derived from pitchblende show a strong and characteristic yellow-green fluorescence under ultraviolet light.

In every outcrop of pitchblende, numerous secondary uranium minerals form as coatings on the pitchblende and the adjacent rocks, or the disintegration products may be noted filling crevices and cavities. Some of the strongly fluorescent secondary uranium minerals are often present in the outcroppings of pitchblende ores in substantial amounts, and include autunite, torbernite, uranophane, zippeite, schroëckerite (dakeite), chalcocite, and uranocircite. Carnotite is one of the secondary uraninites which fails to fluoresce, but can be readily recognized by its characteristic canary-yellow color, and its occurrence in and association with sandstones. *Fluorescent Light and Its Applications*, Dake and De Ment, includes a detailed discussion of the fluorescence of the uranium minerals.

Failure to note fluorescent uranium minerals in the field may not mean the absence of pitchblende or other commercial uranium minerals. On the other hand, noting the presence of the characteristically fluorescing uranium minerals, may be taken as a certain criterion that uranium is present. Additional work would be required to prove or disprove the presence of a commercial body of uranium ore. Rock specimens picked up as surface "float" and suspected of being uraniferous, may carry coatings or pockets of fluorescent material not apparent to the eye. Specimens of this kind may be tested with advantage under ultraviolet light. In general, the use of a portable ultraviolet light for field work

offers a valuable adjunct to other recognized methods of prospecting. The outcroppings of known deposits of uranium ores, which contain fluorescing material may be traced by the aid of ultraviolet light. The fluorescent secondary uranium minerals will fluoresce with all types of ultraviolet light units, but those giving short wavelength radiations, and fitted with a filter of the proper type will give best results. Once the characteristic fluorescence of uranium minerals is fixed in the mind, the color will be readily recognized in the field.

Since the radioactive uranium minerals accelerate the rate of discharge of static electricity from a charged body, an instrument known as an electroscope may prove valuable as a means of locating and tracing deposits of uranium ores. The electroscope may also be used for quantitative determinations of the amount of uranium (and radium) in a hand sample.

At the Great Bear Lake, Canada pitchblende mines considerable use has been made of the Geiger-Mueller counter in surface prospecting to trace the probable extent of the ore-bearing veins. This instrument offers an extremely sensitive and accurate means of detecting the radioactive radiations from uranium ores. At Great Bear Lake the Geiger-Mueller counter fully demonstrated its practical usefulness in prospecting uranium deposits. It was thought that the device might prove of service in conjunction with hand picking the ore in the mill, but it was found impracticable to shield it effectively enough from random radiations to permit its use for this purpose.

Photographic film is affected by the radioactivity of uranium ores, and this method may be used in a qualitative manner in the identification of suspected samples of ore. Frank L. Hess of the United States Bureau of Mines calls attention to the fact that a positive test for radioactivity is not a con-

clusive test for the presence of uranium and radium. Mesothorium, derived from thorium, will also act on a photographic film. Tests for radioactivity will therefore show only whether the specimen contains uranium and radium, or thorium and mesothorium, or all four elements. The appearance of the sample will generally determine which of the elements are present, but in case of doubt, chemical tests are required.

To test a sample for uranium or radioactivity, lay the mineral to be tested on a film or plate holder containing an unexposed film or plate. If uranium is present in any considerable quantity the plate will be acted on within a period ranging from twelve to forty-eight hours, the time depending directly upon the quantity of radioactive matter in the specimen. A rich and nearly pure specimen of pitchblende will affect the film within twelve hours, while a very lean sample like the uraniferous moss agate of Wyoming or the fluorescent hyaline opal from North Carolina, will require weeks of exposure. A metallic object like a flat key or coin placed between the specimen and the film will appear in outline after the film is developed in the usual manner. Irregular mineral specimens may be sawed to obtain a flat surface prior to exposure to film. The flat surface will give a sharper and clearer outline of the radioactive areas within the specimen. Attention is called to the fact that a false radiograph may be obtained by the effects of pressure upon the film. In exposing a film to a specimen, the film placed in a film holder will eliminate the possible error of exposure by pressure.

Another means of noting deposits of uranium minerals is by the bright colors of many of the secondary uranium minerals. Pitchblende and other primary uranium ores, taken from or near the surface are often heavily coated with bright yellow, green, or orange colored secondary uraninites. Below the zone of oxidation and at depth these color coat-

ings are not present. Hence ore bodies of uranium minerals, if they outcrop, may be recognized by the color coatings and by the fluorescence of the secondary uraninite.

Uranium ores are frequently irregularly distributed within an area or deposit, hence prospecting is important even after commercial development is under way. In vein deposits, such as those of Great Bear Lake, Canada; Cornwall, England; and the Belgian Congo, the problem of tracing the uraniferous veins may be somewhat simpler than it is in the patchy deposits of carnotite of Utah and Colorado. The pitchblende found in the granite pegmatites of the New England states, North Carolina, Colorado, and elsewhere usually occurs in small masses or "patches." But in any type of deposit there may be local differentiations in the appearance or the associations of minerals which constitute and aid in following the ore.

While no specific rules can be given as a guide in the search for deposits of uranium ores, the following generalizations may prove of value to the prospector. Primary uranium bearing ores are associated with granitic rocks, which may or may not be metamorphosed schists or gneisses. Pitchblende frequently occurs in pegmatite dikes. The secondary uranium bearing minerals are found associated with the primary ores, but may also be found in sedimentary formations. Pitchblende in a granitic formation is considered as an "original" or primary deposition, while the carnotite of Colorado and Utah has been water transported and is looked upon as a secondary mineralization within a formation with which it has no geological relationship.

The specific gravity of the rich primary uranium ores, like pitchblende is usually high, often from 7 to 9.7. The specific gravity of the secondary uranium minerals is usually about 3.5, but is lower in some instances. Samples of ordinary black colored rock, like the igneous rocks rich in ferroman-

ganese minerals, are sometimes taken for possible pitchblende bearing specimens. The specific gravity of ordinary igneous rock is usually considerably less than pitchblende, the two can be readily distinguished on the basis of gravity in the hand size sample. The prospector searching for deposits of uranium minerals should become familiar with the appearance and properties of at least the important species.

THE PHYSICS OF URANIUM

The Nature of the Uranium Atom

THERE are two important parts of the uranium atom. One, the outer shell composed of many electrons, is mainly of interest to the chemist since these govern the chemical properties, that is, determine the type and extent of combination which will occur between uranium and other elements. The chemical properties of uranium, therefore, can be ascribed to the arrangement and action of the electrons outside the nucleus.

Uranium isotopes, with the same atomic number but of different atomic mass, have the same number and configuration of electrons and are therefore probably identical from a chemical standpoint. Uranium belongs to Group Six the chromium series of elements in the periodic system, and is the terminal member of the series. The elements in Group Six which are closely related to uranium from a chemical standpoint are chromium, molybdenum, and tungsten.

The electronic structure of uranium is intricate, as would be expected, since it is the most complex element. The electronic structure of uranium was elucidated by Sidgwick and Stauer as:

$2/2,2,4/2,2,4,4,6/2,2,4,4,6,6,8/2,2,4,4,6/2,2,4,5/1$

whereas M. Smith (1925) ascribed to uranium the following electronic structure:

$2/2,2,4/2,2,4,4,6/2,2,4,4,6,6,8/2,2,4,4,6/2,2,4/(4,2)$

or with two alternative endings for the sixth and seventh quantum groups: $2,2,4,0,2(2,2)$ or $2,2,4,0(2)$.

Apparently there is no difference of opinion concerning the structure in the subgroups.

In 1934 A. Grosse gave two possibilities concerning the nature of the chemical properties the transuranic elements would have. It is noteworthy that Grosse gave the electronic distribution of uranium, along with other elements, according to the two bases on which the deductions were made.

The chemical properties of elements 93 and 94, i.e., transuranic elements, were deduced according to the periodic law of Mendeleef and on the basis of the Bohr theory. In the former the electron distribution of uranium resulted from analogies with lower homologs given in the periodic system. In the latter the electron distribution of uranium was based on Bohr's "second group" of rare earths.

While the electronic structures for uranium given by Grosse are unique, by the check they provide, it is pointed out that the transuranic elements, instead of having properties like eka-rhenium and eka-osmium (from the periodic system) seem to be more on the order of uranium, the series being analogous to rare earths but chemically dissimilar to them.

The second part of the uranium atom is the nucleus. This is of chief interest from the standpoint of uranium fission and processes which may otherwise be grouped under the heading of nuclear physics. Uranium has an atomic number (Z) of 92. This means that the total number of protons in the nucleus is equal to 92. However, neutrons are also present in the nucleus of the uranium atom. Their number will vary according to the particular isotope of uranium.

The number of neutrons in the nucleus of the uranium atom is A minus Z , where A is the mass number of the isotope, e.g., 238, 235, or 234. Mass number is used to distinguish individual isotopes from atomic weight, the latter term being used by the chemist to denote the weight of naturally occurring uranium. Ordinary uranium, as found in nature, is comprised of a mixture of the various isotopes, the

relative amounts of which might vary according to the source as often times is the case with other elements. This, however, has not been demonstrated with certainty for uranium by experimental methods.

ELECTRONIC STRUCTURE OF URANIUM

Modified, after Grosse

<i>Quantum Numbers</i>		<i>Based on Periodic System</i>	<i>Based on Data of N. Bohr</i>
<i>n</i>	<i>l</i>		
1.....	s.....	2.....	2
2.....	{ s.....	2.....	2
	{ p.....	6.....	6
3.....	{ s.....	2.....	2
	{ p.....	6.....	6
	{ d.....	10.....	10
4.....	{ s.....	2.....	2
	{ p.....	6.....	6
	{ d.....	10.....	10
	{ f.....	14.....	
5.....	{ s.....	2.....	2
	{ p.....	6.....	6
	{ d.....	10.....	10
	{ f.....		1
6.....	{ s.....	2.....	2
	{ p.....	6.....	6
	{ d.....	4.....	4
	{ f.....	(5).....	
7.....	s.....	2.....	1
		(1)	
Highest Valency.....		6.....	6

It follows, therefore, by applying the above equation that the nucleus of uranium with a mass number of 238, the most abundant type of the element, consists of 92 protons associated with $238 - 92$ or 146 neutrons. Likewise, the nucleus

of the important isotope with a mass number of 235 is composed of 92 protons and $235 - 92$ or 143 neutrons. And the light and scarce uranium isotope which has a mass number of 234 has a nucleus comprised of 92 protons which are associated with $234 - 92$ or 142 neutrons.

The atomic number (Z) of uranium, 92, is interesting from two aspects. In addition to revealing pertinent information about the two types and relative abundances of the particles in the nucleus it also denotes the number of electrons outside the nucleus of the neutral uranium atom. As well as being composed of $92 + (A - 92)$ particles of two sorts in the nucleus there are also 92 electrons outside the neutral atom. On this basis the three chief isotopes of uranium can be considered as comprised of a definite number of three different kinds of atomic particles, electrons, protons, and neutrons.

STRUCTURE OF URANIUM ATOMS AND NUCLEI

	<i>Mass Number</i>		
Isotope.....	238.....	235.....	234
Protons in the nucleus.....	92.....	92.....	92
Neutrons in the nucleus.....	146.....	143.....	142
Total nuclear particles.....	238.....	235.....	234
Extranuclear electrons.....	92.....	92.....	92
Total particles in the			
U_o atom = $92 + (A - 92)$	330.....	327.....	326

The two parts of the uranium atom, its nucleus and outer shell of electrons is, when in the tetravalent state, about two Angstrom Units in diameter. The nucleus, however, occupies only a very small fraction of the volume of the entire atom, probably having a radius of about 10^{-12} cm. The nucleus of the uranium atom possesses angular momentum due to spin and also possesses magnetic moment.

At the Research Institute for Physics in Stockholm, Dr. Lise Meitner conducted investigations on the cross-sections

of atoms of the various elements involved in nuclear fission. Dr. Meitner, whose studies on this subject were carried on early in 1940, is the woman scientist who first suggested to Otto Hahn that his experiments actually demonstrated the fission of the uranium nucleus. The investigations are important in nuclear physics since they aid in determining whether neutrons will be captured by the nucleus or whether they will be scattered.

According to the studies by Meitner, the nucleus of the lead atom has a cross-sectional area of 2.5 units with thorium being over twice as large, i.e., 6.0 units. Uranium with a mass of 235 has a cross-sectional area of 1.5 units, being considerably smaller in comparison with the others and therefore much more difficult to strike with neutrons. The exact values which resulted from this study are given in the accompanying table.

CROSS-SECTIONAL AREAS OF ATOMIC NUCLEI

<i>Element</i>	<i>Mass</i>	<i>Value (sq. cm.)</i>
Lead.....	-	2.5×10^{-24}
Thorium.....	-	6.0×10^{-24}
Uranium.....	235.....	1.5×10^{-24}

In all neutral uranium atoms the number of electrons, 92, exactly balances the number of protons, 92. Therefore, the difference in mass is due to the neutrons in the nucleus, these each of approximate unit mass (1.008).

The mass defect of uranium is defined by $\Delta = M - A$ where Δ is the mass defect, M the atomic weight (238.07), and A its mass number (234, 235, and 238). Therefore, the mass defect for the three isotopes of uranium would be $238.07 - 238.00 = 0.07$; $238.07 - 235.00 = 3.07$; and, $238.07 - 234.00 = 4.07$. The packing fraction is defined by $P = \Delta/A$ and its values are the mass defect per elementary particle in the nucleus.

The Atomic Weight of Uranium

The atomic weight of uranium was originally thought to be 120. However, it required the great prognosticator of chemistry, Dmitri Mendeleef to correct this miscalculation. He pointed out that there was no place in the periodic table for a trivalent element of atomic weight 120. He emphasized that uranium resembled chromium, molybdenum, and tungsten and suggested that the atomic weight be doubled, or at least re-determined. Mendeleef's work in 1872 was based on analogies with elements in Group Six.

Mendeleef predicted and described with accuracy the oxides of uranium, the true nature of which was not known with certainty at the time. He described uranous oxide as UO_2 ; urano-uranic oxide as U_3O_8 or $[\text{UO}_2 \cdot 2\text{UO}_3]$; and, UO_3 as uranic oxide. The prediction included the facts that uranium was both tetravalent and hexavalent. These incredible predictions were later confirmed by the determination of specific heats, the application of Dulong and Petit's Law, and by vapor density determinations on uranium halides.

Early determinations of the atomic weight of uranium were obviously erroneous because the oxide of the metal was mistaken for the pure element. However, this does not affect the analytical data. Of historical interest are the determinations of atomic weight by J. Berzelius, J. Arfvedson, and R. Marchland. Other earlier measurements vary so widely as to be valueless.

In 1902 Richards and Merigold analyzed uranium bromide, UBr_4 . They determined the bromine as silver bromide. The value obtained was high, being 238.4 and discrepancies were ascribed to the reactions which occurred when glass apparatus was used. Later, using silica apparatus Hönigschmid (1904) relied on the same procedure for an

atomic weight determination. The result of this determination was somewhat less than the value obtained by Richards and Merigold.

In 1916 Hönigschmid and Horowitz used the same procedure again and obtained 238.17 as the atomic weight of uranium. This was adopted in 1925 by the International Committee on Atomic Weights. Hönigschmid and Horowitz used uraninite of different ages to note the effect, if any, of age upon the atomic weight of uranium.

In 1936 Hönigschmid and Wittner investigated the ratios $\text{UCl}_4:4\text{Ag}:4\text{AgCl}$ and $\text{UBr}_4:4\text{Ag}:4\text{AgBr}$. For this set of determinations minerals from different parts of the world were used as sources for uranium. The halides of uranium were prepared by heating the oxide with sugar charcoal in an atmosphere of nitrogen, together with chlorine or bromine.

VALUES GIVEN FOR THE ATOMIC WEIGHT OF URANIUM

From 1894 to 1941

239.6.....	1894-1895
239.59.....	1896-1899
239.6.....	1900-1902
238.5.....	1903-1915
238.2.....	1916-1922
238.17.....	1925
238.14.....	1931-1936
238.07.....	1937-1941

The first sublimate obtained from this was resublimed into a weighed quartz tube, all being contained in a quartz bottling system. It was found that material which had been fused after sublimation appeared to yield slightly higher and less consistent results than when final fusion was omitted because of the dissociation and loss of halogen which probably occurred during fusion. The final value obtained by these

determinations was 238.07, a value slightly lower than the previous determinations.

The Isotopes of Uranium

It is rather evident, especially from the extensive popularization, that the isotopes of uranium are of astonishing significance with the rapid developments in uranium fission and related phenomena. Three isotopes of uranium have been isolated and their relative abundances determined.

The first determination of the uranium isotopes was the qualitative record obtained by Francis Aston, in 1931, who used the mass-spectrometer for his investigations. Aston showed that at least 97 per cent of the uranium atoms had a mass of 238. In 1935, Dempster estimated that the isotope uranium 235 probably was present in uranium 238 in amounts less than one per cent. The actual quantitative and pioneering studies in the determination of the amounts of uranium isotopes, as well as the investigation which resulted in the discovery of a still lighter member, uranium 234, was by A. O. C. Nier of the University of Minnesota. Nier's classical work has been carried on since 1938.

The procedure used by Nier consisted of passing vaporized uranium tetrachloride or tetrabromide into the chamber of a mass-spectrograph, from which the relative amounts of the three isotopes could be ascertained. The close agreement between average values for the three specimens of minerals used indicated that the ratio does not depend on the source of uranium, variation being due to systematic errors in calibration, discrimination of apparatus against different mass numbers, and so on.

Following are the ratios determined by Nier :

$$\frac{U^{238}}{U^{235}} = 139.0 \quad \text{and,} \quad \frac{U^{238}}{U^{234}} = 17,000$$

The limit of error on the last determination being 10 per cent.

$U^{238} : U^{235}$ RATIO IN DIFFERENT MINERALS

After A. O. C. Nier

KOLM (Sweden)		URANINITE (Ontario)		DAKEITE (Wyoming)	
<i>Ratio</i>	<i>Ion Used</i>	<i>Ratio</i>	<i>Ion Used</i>	<i>Ratio</i>	<i>Ion Used</i>
139.0.....	I	140.8.....	III	139.7.....	III
139.4.....	I	135.3.....	III	139.7.....	III
139.1.....	I	135.3.....	III	136.6.....	III
139.4.....	I	142.3.....	III	138.0.....	III
137.5.....	II	137.1.....	III	137.8.....	III
138.0.....	III	139.4.....	III	138.2.....	III
138.8.....	III	139.1.....	III	141.3.....	IV
140.7.....	IV	139.7.....	III		
		139.6.....	III		
		139.4.....	III		
		140.3.....	IV		

Averages

139.0.....138.9.....138.8

Type of Ion Studied: I = U^+ in UCl_4 ; II = UCl^+ in UCl_4 ; III = U^+ in UBr_4 ; and, IV = UBr^+ in UBr_4 .

The investigation also included a search for other isotopes. Although none was found it was possible to set the upper limits of abundance for the following:

$$\frac{U^{238}}{U^{242}} ; \frac{U^{238}}{U^{241}} ; \frac{U^{238}}{U^{240}} \text{ as } 65,000$$

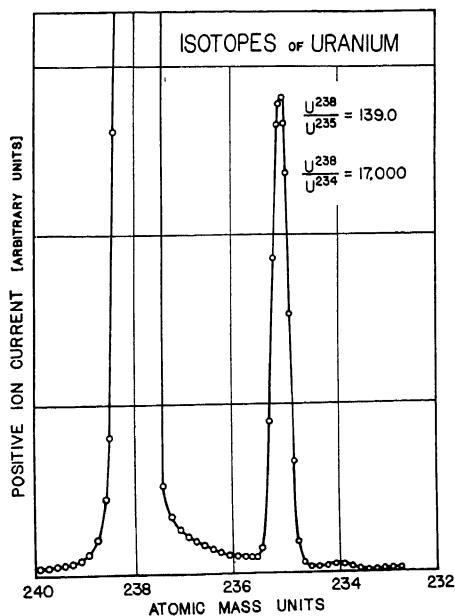
as well as,

$$\frac{U^{238}}{U^{239}} ; \frac{U^{238}}{U^{237}} \text{ as } 12,000$$

and,

$$\frac{U^{238}}{U^{236}} ; \frac{U^{238}}{U^{233}} ; \frac{U^{238}}{U^{232}} ; \frac{U^{238}}{U^{231}} \text{ as } 35,000$$

By the method of magneto-optic analysis eight isotopes of uranium were indicated by the experimental results of R. Goslin and Fred Allison of the Alabama Polytechnic In-



Mass spectrum showing the relative abundance of isotopes of uranium. The points for the curve are obtained by plotting positive ion current passing through the exit slit of the analyzer, as a function of the energy of the ions in a constant magnetic field. A definite relation exists between the energy and the mass of the ions collected. The width of the peaks is due to focusing imperfections and the finite width of the slits used. (Dr. Alfred O. C. Nier, University of Minnesota)

stitute in 1939. In the search by Nier twelve possible isotopes are mentioned (see previous data). However, only three of these were demonstrated, i.e., U^{238} , U^{235} , and U^{234} ,

the others having only their upper limits of abundance set. But of the twelve isotopes mentioned in this investigation four are transuranic, i.e., U^{239} , U^{240} , U^{241} , and U^{242} . This leaves the possibility of the existence of eight isotopes, three being known with certainty.

Therefore, the eight isotopes indicated in the investigation of Goslin and Allison appear to check exactly with the same number mentioned in Nier's research. The existence of transuranic elements and the work of Fermi on elements with atomic masses greater than the atomic mass of U^{238} is mentioned elsewhere. Regarding the possible uranium isotope 237 which was not demonstrated, but only indicated on the basis of comparatively small evidence in both studies are the following researches by Wahl.

In 1941 Walter Wahl of the University of Helsingfors reported the discovery of mass line 237. This line was obtained from some old minerals (in a geological sense) of the tantalum-columbium group during mass-spectrographic investigation (see the chapter on the minerals which bear radioelements). Mass line 237 had never been obtained from any other material although a great number of minerals were investigated by Wahl with the same instrument and under the same conditions.

According to Wahl, so far as is known mass line 237 does not belong to any now known chemical element or isotope. Likely mass line 237 does not belong to any isotope of 90 thorium or 92 uranium and since it is found in only one group of minerals to which neither of the above elements belong it is probable that it belongs to an isotope of the chemical element of the odd number 91, eka-tantalum. The writers wish to point out that both thorium and uranium often do exist in the tantalum-columbium group of minerals as impurities.

According to Wahl, mass line 237 probably belongs to an

element which is a member of a so far unknown radioactive series. Because of its odd mass number it cannot belong to the uranium or the thorium series, these all having even mass numbers. However, members of the actino-uranium series all have odd mass numbers but these are all $4n$ smaller than 235 with $n = 1$ to 7, the ultimate product in the disintegration being lead 207.

Separation of Isotopes

The separation of the uranium isotopes from each other has been a source of considerable difficulty. Although the mass-spectrograph allows separation of very small amounts, the production of any or all of the uranium isotopes in pure form and in large amounts has not been attended with marked success. A number of methods used on the isotopes of other elements hold promise and with further investigation results become increasingly encouraging.

It must be remembered that analogies are notoriously unsafe guides. This becomes especially evident when applied to the separation of the uranium isotopes. Francis W. Aston, who won the Nobel Prize for his work on isotopes and mass spectra, appropriately considered the following in 1933. He regarded isotopic separation in the light that the possibility of isolation of isotopes to any reasonable extent raises questions of significant importance to applied science. This is exactly the case in the separation of the uranium isotopes.

Thermal diffusion is a method which has been used with satisfactory results considering the variety of elements to which it has been successfully applied. The thermal diffusion method was developed independently by two investigators, Enskog in 1911 and Chapman in 1916. In this method a mixture of two gases of different molecular weights is allowed to diffuse freely throughout a tube with ends at dif-

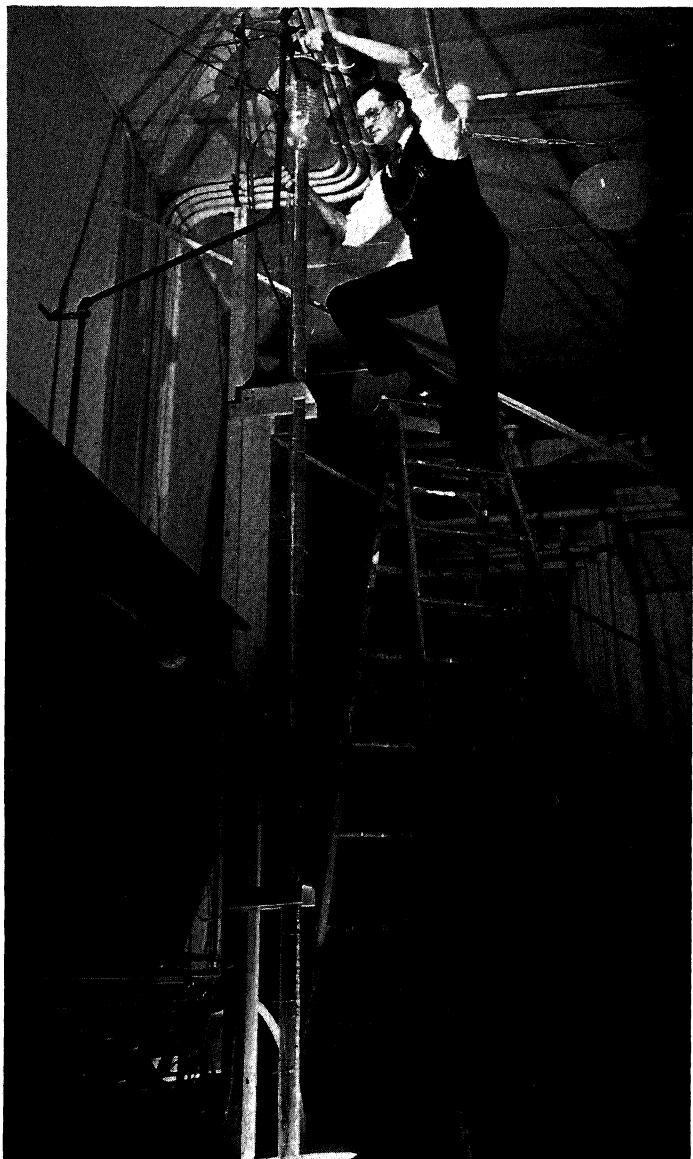
ferent temperatures. After equilibrium is attained there will be a slight excess of the heavier gas at the cold end and the lighter gas at the hot end. Refinements of the basic principle are denoted by the many different modifications of the instrument which have been used by various investigators.

For example, in the Research Laboratory of the General Electric Company K. H. Kingdon and H. C. Pollock have used equipment 14 feet high. The principle parts are two long glass tubes, one inside the other, and a gold wire extending from top to bottom in the inner tube. This tube contains in gaseous form the material to be separated and is kept at a fixed temperature by passing steam through the outer tube. When the gold wire is heated the lighter atoms rise to the top and the heavier atoms descend to the bottom where they are collected. A gold wire is used because a baser metal might be attacked or consumed by the material being studied. A larger wire circling the outer tube is used only to bake out the apparatus, a standard vacuum practice.

Two German investigators, Clusius and Dickel, have been among the foremost pioneers in use of thermal diffusion methods. These investigators have successfully separated the isotopes of such elements as chlorine, krypton, and neon. The substance used in investigations with thermal diffusion equipment on uranium is the hexafluoride, one of the few if not the only known compound of uranium that exists in gaseous form.

When a substance in combination or in the pure form is ionized and passed into a field of energy, i.e., a magnetic or electric field, and diverted as a beam from its course, the heavier particles will be diverged the least, while the lighter particles will be diverged the most. In essence, this is the principle of mass ray separation and is the basis for the comparatively recent science of mass-spectroscopy.

The beam may be in the form of positive rays, these being



The General Electric Company thermal diffusion tower, used in studies on the separation of the isotopes of various elements.

most effective but anode (negatively charged) rays may also be used. In both the amount of separation is qualitatively great but quantitatively extremely small, serving primarily for purposes of investigation. In both the beams are accelerated by a uniform field and separated by simple semi-circular magnetic or electric focusing, the former being preferred.

Separation by diffusion through a membrane was described in 1896 by Lord Rayleigh. Separations through porous membranes can be hypothesized on the basis of knowledge about chemical kinetics, colloids, and mechanisms which occur when gases and liquids are mixed. Separation by diffusion is supposed to occur through a porous material, the diffusion velocity taking place according to the mass of the molecules in the system. The velocity of diffusion is proportional to the square root of the mass and it follows that gases which differ considerably in mass would have to be used. This method is applicable to hydrogen since the difference with other isotopes would be so small as to reduce the product to a very small quantity.

Electrolytic separation. This method is used for the concentration and often for the isolation of pure deuterium, i.e., heavy hydrogen, with a marked degree of practical success. In electrolysis the light isotopes leave in the liberated gas, a greater abundance of the heavier isotope remaining in the liquid, i.e., water, under electrolytic treatment. As is apparent, the electrolytic method is limited to isotopes which can be changed from combination, generally in the liquid state to the gaseous state by the action of electrical currents.

When a heterogeneous fluid, such as a system containing isotopes, is subjected to a gravitational field the heavier particles tend to concentrate in the direction of the field. An illustration of this is in long tubes of water which remain undisturbed, in a vertical position, for considerable periods of

time. The result of this is a greater concentration of deuterium at the bottom of the tube. However, by not relying on the feeble gravity of the earth for separation it is possible to use the enormous gravitational fields developed in ultra-centrifuges for studies on isotope separation. The term pressure diffusion is applied to this technique.

J. W. Beams, instrumental in designing and study of super-centrifuges, has used a gold plated device to study the utility of this principle for concentrating and/or isolating isotopes of the various elements. Rotors which revolve at tremendous speeds are now possible by a recently developed principle. This is the suspension of the centrifuge head by a magnetic field in a very low vacuum and spinning by rapidly oscillating surges of power. The rotors in centrifuges of this type are practically frictionless.

Photochemical separation is a most striking means for the segregation of atomic particles which vary in mass. The photochemical method was first suggested by Merton and Hartley in 1922. It entertains the following considerations. In a mixture of chlorine and hydrogen combination occurs when light falls upon the two. Combination between the two gases is often accompanied by an explosion. The combination is assumed to be due to the activation of atoms of hydrogen or of chlorine since the two will not combine at all, or only very slowly, in darkness.

Should it be the chlorine, it is pointed out that the wavelength of light required to cause combination of one isotope would vary slightly from the wavelength of light required to cause the other isotope to combine. Thus, by selective absorption by one chlorine isotope of its particular exciting wavelength, without the presence of the other wavelength, a corresponding selective combination might result. Although this method works out satisfactorily in theory it has not been

confirmed experimentally to the extent of allowing separation on a practical scale.

Isotopes may be different from a chemical standpoint. This is shown especially in the isotopes of hydrogen, viz., deuterium where deuterammonia, deuterammines, and other well defined compounds with isotopes in the structure are known. It requires, however, considerable experimental evidence to establish the chemical differences of isotopes and generally the result of such differences is so slight that separation for practical purposes cannot be accomplished in more than a few select instances. Lindemann, in 1919, developed this method theoretically but on the basis of present knowledge it cannot be applied extensively to the isotopes of uranium.

Slight differences in vapor pressure as a means of separating isotopes was also developed theoretically in 1919 by Lindemann. Fractional distillation has been mentioned by others as a tool for concentrating atoms of different mass. The method, however, is apparently restricted to the nature of the element and its compounds which might be subjected to fractional distillation.

Low pressure evaporation has actually been used to isolate the various isotopes of mercury. In 1920 Bronsted and Hevesy worked out this method. It depends on that fact that if a liquid containing isotopes is allowed to evaporate the number of light atoms escaping will be greater than the number of heavier atoms. This is in inverse proportion to the square roots of the masses of the isotopes. The pressure above the surface is kept low so that the light particles will not return to the system (cf. foregoing data of Lindemann).

Free evaporation. In this the separation is along the same principles as low pressure evaporation and fractional distillation. The free evaporation technique was used by Bronsted

and Hevesy for studies on the isotopes of chlorine. The procedure consisted of evaporating a solution of hydrochloric acid in water at -50° C. and allowing the vapor to condense on a surface cooled by liquid air.

The application of evaporation and, in general, the change from the solid or liquid phase to the gaseous phase to separation of uranium isotopes appears to be restricted by the few compounds of uranium suitable for such use. The main gaseous uranium compound is uranium hexafluoride and use of this is limited by its reactivity.

Electron impact has been suggested for the separation of isotopes. In this it is postulated that the lighter isotopes are more strongly urged toward the anode when electrons pass through an inert gas in a low pressure discharge tube.

Fractional crystallization was suggested in 1923 by Atkinson for separation of isotopes. Also, the action of light on metallic chlorides may be a mechanism by which separation could be accomplished, this being suggested by Renz in 1921. Neither of these has been attended by a marked degree of success.

The zeolites were recently suggested as a medium with which the separation of isotopes could be accomplished. The zeolites are naturally occurring sodium aluminum silicates, NaAlSiO_4 . Permutite is a manufactured product of the same nature and has been used by J. G. Dean for separating the isotopes of light elements such as potassium and lithium. When water which contains calcium or other ions slowly passes through thick layers of this material, the sodium in the zeolite is replaced by calcium and the water is freed of the latter. The zeolite can be regenerated by allowing a concentrated sodium chloride solution to pass through it, the same process occurring again with the sodium replacing the calcium.

Dean concentrated the isotopes of the lighter elements, i.e., potassium and lithium, by the zeolite method. The procedure for potassium consisted of passing a 3% aqueous solution of potassium chloride through a column of zeolite about one meter in length. Potassium chloride solution yielded from the zeolite by regeneration by sodium chloride, after only one treatment, contained several per cent more of the light isotopes than the solution introduced initially. The nitrogen isotopes can be concentrated by the zeolite method.

Ionic Migration has been suggested as a means for separating isotopes. In this method the isotope ions are allowed to migrate through a gel. The assumption is that isotope ions, with their different masses, will traverse a gel at different rates and result in separation or concentration. Negative results have been obtained so far in use of this principle and the conclusions of many investigators on the basis of experimental studies, are that ionic mobilities are dependent only on atomic volume and not on atomic mass.

Isotopes might be separated on the basis of the following postulation. The element to be subjected to separation or concentration is introduced into a gel or other medium in combination with iron, e.g., as the ferrocyanide. By subjecting these ferriferous molecules to a magnetic field, in order to accelerate their migration linearly through the gel, separation or concentration might be accomplished. The basis is on the assumption that molecules involving combination of a light isotope with iron would travel at different rates through a medium than heavier isotopes in the same combination. Investigation on the magnetically accelerated passage of highly paramagnetic molecules involving isotopes through viscous media presents some interesting possibilities.

The segregation of isotopes, i.e., atomic particles of different mass by magnetic means is the principle involved in the

mass-spectrometer mentioned previously. The mass-spectrometer differs from the foregoing postulation in that in the spectrograph ions or charged particles are subjected to fields of energy. In the above postulation chargeless molecules are subjected to a magnetic field and are attracted in lieu of their magnetic susceptibility, a threshold value perhaps being involved in separations of this sort.

The Natural Radioactivity of Uranium

Much in the present state of man can be directly attributed to a black, apparently trivial and uninteresting mineral-pitchblende. This extraordinary substance first yielded uranium to Klaproth. Uranium, in turn, resulted in the discovery of radioactivity by Henri Becquerel. From radioactivity and pitchblende the Curies were led to radium and polonium and a new era in science. This resulted in radon with Andre Debierne discovering actinium and actinon in slightly ramifying researches. And at about the same time Ramsay used cleveite, a variety of pitchblende, to demonstrate the existence of helium on the earth. Protoactinium followed by less than two-score years. Yes, the mere "schwarzpecherz" has come into its own.

It is difficult, if not impossible, to say which will be of the most importance in the future. The phenomenon of radioactivity and the new lease on life it has given science is obviously of utmost significance. But who can tell whether radium, natural radioactivity, and its pioneers are to be regarded of incidental import in favor of uranium, *nuclear fission*, and its pioneers?

Freshly prepared uranium emits alpha particles. Uranium with its atomic weight of 238, after losing an alpha particle, i.e., a helium ion of mass 4, is degenerated into an element with a mass of 4 less than the original uranium 238. In

approximation this illustrates radioactive disintegration. However, in radioactive transformations a beta particle, i.e., an electron, may be given off, this having practically a negligible mass with a new radioactive element being formed but of the same isotopic mass. In the mechanism which follows each element breaks down with the emission of a particle with each element having its individual characteristics and life.

Uranium might be called the mother of radium but more strictly accurate is that ionium is the mother with uranium only a maternal ancestor. But uranium is just one of many natural radioactive elements. Practically all of these have atomic numbers between 81 and 92 and may be grouped into three series, the uranium-radium series, the thorium series, and the actinium series. In each of the series, which are themselves comprised of many radioactive elements, any one of the members may be traced back to a parent element by transformations which involved the emission of an alpha or a beta particle as described above. The *uranium-radium series*, to which both uranium and radium belong, is contained in the table on page 70. It will be noted that lead is the end-product in the disintegration of the uranium-radium series.

It follows, therefore, that uranium and radium, both being in the same dynamic system, i.e., radioactive series which continually breaks down, would over a period of time, reach an equilibrium. This is exactly the case, for in uranium minerals the radium, which is invariably present, is in a definite ratio to the uranium.

The ratio which exists between uranium and radium in mature minerals is defined by Boltwood's Constant and states that one part of radium is always present for every 3,400,000 parts of uranium. Exceptions to the case are due, however, to leaching-out of either radium, or uranium, or to insuffi-

cient time to allow an equilibrium to be attained. The young uranium minerals are almost always of the secondary type, and formed by the alteration of primary uranium minerals like uraninite and pitchblende.

URANIUM-RADIUM SERIES OF NATURAL RADIOACTIVE ELEMENTS

<i>Element</i>	<i>Atomic Weight</i>	<i>Atomic Number</i>	<i>Isotope</i>	<i>Average Life</i>	<i>Radiation</i>
Uranium I.	238.	92.	U.	6.4×10^9 yrs.	alpha
Uranium X ₁	234.	90.	Th.	35.4 days.	beta
Uranium X ₂	234.	91.	Pa.	1.64 min.	beta
Uranium Z.	234.	91.	Pa.	9.7 hrs.	beta
Uranium II.	234.	92.	U.	4.3×10^5 yrs.	alpha
Ionium.	230.	90.	Th.	1.2×10^5 yrs.	alpha
Radium.	226.	88.	Ra.	2295 yrs.	alpha
Radon.	222.	86.	Rn.	5.5 days.	alpha
Radium A.	218.	84.	Po.	4.4 min.	alpha
Radium B.	214.	82.	Pb.	38.7 min.	beta
Radium C.	214.	83.	Bi.	28.5 min.	beta
Radium C'.	214.	84.	Po.	10^{-6} sec.	alpha
Radium C''.	210.	81.	Tl.	1.9 min.	beta
Radium D.	210.	82.	Pb.	27.4 yrs.	beta
Radium E.	210.	83.	Bi.	7.0 days.	beta
Radium F.	210.	84.	Po.	202 days.	alpha
Radium G.	206.	82.	Pb.	—————	—————
<i>(lead)</i>					

The thorium series begins with thorium and is in many respects like the uranium-radium series. The thorium series also ends in lead like the uranium-radium series. Originally it was thought that the third series, the actinium series, comprised an independent group of radioactive elements. However, it has been learned that a radioactive isotope of uranium called actino-uranium, with a mass of 235, gives rise to the actinium series. In this series, as in the others, the end-product is an isotope of lead.

ACTINIUM SERIES OF NATURAL RADIOACTIVE ELEMENTS

<i>Element</i>	<i>Atomic Weight</i>	<i>Atomic Number</i>	<i>Isotope</i>	<i>Average Life</i>	<i>Radiation</i>
Actino-uranium	235	92	U	5.7×10^8 yrs.	alpha
Uranium Y	231	90	Th	35.5 hrs.	beta
Protoactinium	231	91	Pa	4.6×10^4 yrs.	alpha
Actinium	227	89	Ac	19.4 yrs.	beta
Radioactinium	227	90	Th	27.3 days	alpha
Actinium X	223	88	Ra	16.2 days	alpha
Actinon	219	86	Rn	5.6 sec.	alpha
Actinium A	215	84	Po	3×10^{-3} sec.	alpha
Actinium B	211	82	Pb	52 min.	beta
Actinium C	211	83	Bi	3.1 min.	alpha
Actinium C'	211	84	Po	7×10^{-3} sec.	alpha
Actinium C''	207	81	Tl	6.8 min.	beta
Actinium D	207	82	Pb	_____	_____
<i>(Lead)</i>					

Transuranic Elements

Elements heavier than uranium may have existed at one time. The explanation as to why they do not exist at present would supposedly lie in their comparatively short lives. This means that elements heavier than uranium, called transuranic elements, may have existed once but these disintegrated rapidly so that the only trace left of them now is uranium. It means further, that uranium may only be an intermediate in a now extinct radioactive series.

It also means that the radioactive series with which we are now acquainted are merely remnants of the series which once may have included any number of transuranic elements. Further, among the light elements only three are known to be naturally radioactive. These, potassium, rubidium, and samarium, may also be remnants, either individually or as a whole of a now extinct radioactive series, the other members

of which have disintegrated due to their comparatively short lives.

Present evidence points strongly toward assumptions of this type. The evidence is the result of predictions and subsequent experimental verification by Enrico Fermi, Nobel Laureate, and his co-workers, E. Amaldi, F. Rasetti, E. Segre, and B. Pontecorvo. The controversy which followed Fermi's hypothesization of the existence of transuranic elements resulted in the discovery of an entire new group of elements heavier than uranium 92.

Fermi actually prepared element 93 by bombarding ordinary uranium of atomic weight 238 with a feeble stream of neutrons, one of which was captured by resonance in the uranium nucleus forming element 93 of atomic weight 239. The new element, as would be expected, was radioactive with a short half-life, hence the assumption of a now extinct series of natural radioactive elements heavier than uranium.

In 1934 A. V. Grosse discussed two possibilities of the chemical properties of the transuranic elements. One, based on the periodic table and analogies with lower homologs has been discredited while the other, based on Bohr's theory appears to be substantiated with reservations. According to N. Bohr (1922) a "second group" of rare elements probably exists somewhere beyond uranium. This group would be presumed to have very similar chemical properties where the additional electron from element to element will be bound to a lower quantum level and not be available as a valence electron.

It is assumed that the filling of the lower quantum level has begun already in uranium. Uranium would then be an analog to cerium in the "first group" of rare earths and transuranic elements 93, 94, 95, and on, all have chemical properties similar to element 91. This would follow from comparison with the first series of rare earths where the chemical properties of Pr, Nd, Sm, and others are nearly

identical with La. In addition, elements 93 and 94 in that case would not have the properties of eka-rhenium and eka-osmium as predicted from the periodic system.

ELECTRON DISTRIBUTION BASED ON DATA OF BOHR

After Grosse

Quantum Numbers		Elements				
		91	92U	93	94	95
<i>n</i>	<i>l</i>					
1	s	2	2	2	2	2
2	s	2	2	2	2	2
	p	6	6	6	6	6
	s	2	2	2	2	2
3	p	6	6	6	6	6
	d	10	10	10	10	10
	s	2	2	2	2	2
4	p	6	6	6	6	6
	d	10	10	10	10	10
	f					
	s	2	2	2	2	2
	p	6	6	6	6	6
5	d	10	10	10	10	10
	f		1	2	3	4
	s	2	2	2	2	2
6	p	6	6	6	6	6
	d	3	4	4	4	4
	f			(5)		
7	s	2	1	1	1	1
Highest						
Valency		5	6	5	5	5
				(6)		

While transuranic elements can be prepared in the laboratory from man-made neutron sources the upper stratosphere contains an abundance of free neutrons. S. A. Korff, in

studies conducted in 1939, found that neutrons are about one-thousand times more abundant 13 miles overhead than at sea level. Also, neutrons occur in the upper regions of the atmosphere by the billions. Korff explained the origin of stratospheric neutrons on the basis of disruption of nitrogen nuclei by cosmic rays. When one nitrogen nucleus is disrupted seven neutrons are liberated. The occurrence of neutrons in the stratosphere makes an interesting correlation with the assumption of the now extinct transuranic elements.

The Induced Radioactivity of Uranium

The conversion of stable atomic nuclei into unstable artificial radioactive isotopes by bombardment with alpha particles, neutrons, deuterons, and protons appears to be a general property of elements extending to all parts of the periodic system. This has been discussed by C. R. Haymaker (1938). Uranium is unique in this respect from two aspects.

In one aspect uranium reacts with the bombarding particle, i.e., the neutron, and fission of the nucleus results with the ejection of a large number and variety of isotopes, energy, and additional neutrons. This is known as nuclear fission and while most characteristic of uranium is also noted in thorium and protoactinium. Nuclear fission is discussed in detail elsewhere herein.

The second unique aspect of uranium is that bombarding particles, in addition to forming unstable transuranic elements, might also form relatively stable heavier transuranic elements, i.e., element 94, which would not decay readily. Both aspects have one thing in common. Both are in the developmental stage and additional experimental evidence is required to place them on a more absolute basis.

It appears that radioactivity cannot be induced in uranium by bombarding with alpha particles. This is based on the fact that the production of radioactivity seems to be limited

to elements of low atomic number, extending no higher than phosphorus with an atomic number of 15. Also, only a few cases of induced radioactivity have been the result of bombardment with protons and uranium is not yet included in this category, boron and carbon being the principle examples. Light elements respond best to treatment with protons.

Deuterons and neutrons are much more efficient for inducing radioactivity in heavier elements. Neutrons are especially effective on uranium, more so than other atomic particles. The reaction(s) between neutrons and uranium are illustrated by the two mechanisms described above which occur when uranium nuclei are bombarded with these neutral fragments of matter.

Induced radioactivity in elements is usually of the beta emission type, i.e., electrons or positrons (positive electrons—see table of subatomic projectiles). However, a few artificial radioactive elements are known that emit alpha particles. In some artificial radioactive elements branching in transformation occurs, e.g., copper and tin, along lines similar to that in natural radioactive disintegration.

SUBATOMIC PROJECTILES

<i>Particle</i>	<i>Symbol ($= {}_Z X^A$)</i>	<i>Z</i>	<i>A</i>
Proton.....	${}_1\text{H}^1$	+1.....	1
Neutron.....	${}_0\text{n}^1$	0.....	1
Electron.....	e^-	-1.....	0
Positron.....	e^+	+1.....	0
Alpha particle.....	${}_2\text{He}^4$	+2.....	4
Deuteron.....	${}_1\text{H}^2$	+1.....	2

C. R. Haymaker has given an excellent general classification which aids in interpreting the effect of nuclear reactions on the nature of atoms. The effect of the addition or the subtraction from an atomic nucleus of subatomic particles (see table) used for changing the nature of atoms is to raise

or lower, as the case may be, the atomic number (represented by Z) and the mass number (represented by A), of a nucleus by an amount equal to Z or A of the particle gained or lost.

The greater part of known nuclear reactions, however, produces a net result which is equivalent to substitution of one type of particle for another within an atomic nucleus. It follows that the effect on A and Z of the nucleus in question must be interpreted from the proper combination of these constants for the particle entering and that leaving. The list gives the subatomic particles used for inducement of radioactivity while the accompanying table outlines the effect of nuclear reactions on the nature of atoms. The chemical nature of the atom formed in any of the processes in the following table will obviously depend on the position of the element undergoing the change in the periodic system.

THE EFFECT OF NUCLEAR REACTIONS UPON THE NATURE OF ATOMS

Modified, after Haymaker

- I. Processes which increase Z by unity.
 - a. Emission of an electron (A remains constant).
 - b. Capture of a proton with emission of a quantum (A increases by one).
 - c. Capture of a proton with emission of a neutron (A remains constant).
 - d. Capture of an alpha particle with emission of a proton (A increases by three).
 - e. Capture of a deuteron with emission of a neutron (A increases by one).
- II. Processes in which Z is unchanged.
 - a. Capture of a neutron with emission of a quantum (A increases by one).
- III. Processes in which Z decreases by unity.
 - a. Emission of a positron (A remains constant).

- b. Capture of a neutron with emission of a proton (A remains constant).
 - c. Capture of a proton with emission of an alpha particle (A decreases by three).
 - d. Capture of a deuteron with emission of an alpha particle (A decreases by two).
- IV. Processes in which Z decreases by two.
- a. Capture of a neutron with emission of an alpha particle (A decreases by three).
 - b. Emission of an alpha particle (A decreases by four).
- V. Processes in which Z increases by two.
- a. Capture of an alpha particle with emission of a neutron (A increases by three).

Crystallinity and Other Aspects

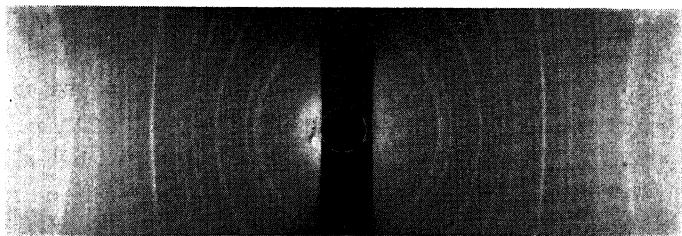
The crystalline structure of uranium was studied extensively in 1937 by C. W. Jacob and B. E. Warren. These investigators determined the structure of the element by the use of X-ray spectrography. Metallic uranium was found, on the basis of X-ray methods, to have an orthorhombic unit cell with axes

$$a : b : c = 2.852 : 5.865 : 4.945 \text{ (A.U.)}$$

Uranium can be considered as a deformed hexagonal close-packed structure with four of the twelve nearest neighbors moved in closer. The number of neighbors and their distances is as follows:

Number.....	2	2	4	4
Distance (A.U.)....	2.76	2.85	3.27	3.36

On the basis of both high electrical resistivity and X-ray spectrograms the uranium structure is not a typical metallic material. A tendency to form four covalent bonds is indicated by the four closer neighbors.



X-ray powder pattern of uranium, obtained by use of Cu K_α radiation ($\lambda = 1.539 \text{ \AA}$). X-ray powder patterns lead to an orthorhombic unit cell. The structure can be considered as a deformed hexagonal close-packed structure with four neighbors closer than the other eight. A cylindrical camera with a diameter of 57.3 mm. was used. (Spectrogram by Dr. B. E. Warren, Massachusetts Institute of Technology)

According to Jacob and Warren the structure is essentially that of a pseudo metal such as antimony or gallium. The comparison of the electrical resistivity of uranium with the values for other elements follows. The determinations are approximate and at room temperature; being $n \times 10^{-6}$

$U = \begin{cases} 32 \\ 62 \\ 76 \end{cases}$	$Sb = 39$
	$W = 5.5$
$Ga = 53$	$Cu = 1.7$
	$Ag = 1.6$

From its position in the periodic table uranium would appear to have the same crystal structure of other elements of its group, i.e., chromium, molybdenum, and tungsten, all of which crystallize body centered cubic. In consideration of the density of these metals this does not hold true. When the values for each are plotted on a graph the densities of chromium, molybdenum, and tungsten which have the same crystal structure fall on a smooth curve while uranium is definitely off the curve.

The structure of uranium appears to be quite different from that of any other element. Neodymium is the only other element which shows any relationship to uranium in

crystal structure and which is in the same column of the periodic table. Neodymium crystallizes hexagonal close packed while uranium has a distorted hexagonal close packed structure.

The embrittlement of uranium by small amounts of aluminum and iron has been studied by H. W. Highriter and W. C. Lilliendahl (1935). These investigators found that electrolytic uranium is embrittled by aluminum in amounts as low as 0.20% and by iron in amounts as low as 0.5%. When in combination the two metals in smaller amounts caused embrittlement. Small amounts of carbide appear to have no adverse effect upon the ductility of uranium. Impurities in uranium were found due to the graphite crucible used in electrolysis and also in the use of impure sodium and calcium chlorides. The effect of various metals on uranium is shown in the accompanying table.

EFFECT OF METALS ON URANIUM

Highriter and Lilliendahl

<i>Additions Made, %</i>	<i>Analysis, %</i>		<i>Character of Metal</i>	<i>Rockwell Hardness</i>
	<i>Fe</i>	<i>Al</i>		
None.....	0.04...	0.01.....	Ductile.....	B-95
0.40 Al.....	0.07...	0.20.....	Brittle.....	B-100
0.50 Fe.....	0.53...	0.10.....	Mod. ductile...	B-102
0.50 Al.....	0.38...	0.32.....	Brittle.....	B-103

As a research tool uranium has been useful as a strong source of monochromatic X-radiation. C. M. Slack studied the properties of uranium for use in anticathodes for X-ray production. By using metallic uranium which had a melting point of 1690° C. K radiation of 0.126 A.U. wave length was produced and an X-ray efficiency of 125 was obtained. The X-ray efficiency was indicated by these studies to be greater than that for both thorium and tungsten, the values for which are 120 and 91, respectively. See Siegbahn's table

which accompanies for data on the X-ray emission spectra of uranium.

In 1934 J. W. Marden studied uranium from a standpoint of its value for use in gas discharge devices. The use of uranium in commercial gas discharge devices is a matter of considerable importance. The potential required to initiate a discharge between two electrodes in a gas is dependent upon the distance between the electrodes, the material, surface condition of the electrodes, the nature, purity, and pressure of the gas. Uranium is so active toward ordinary gases such as oxygen and nitrogen that these gases are rapidly consumed when a discharge is initiated between electrodes of this element so that if impure inert gases are employed, the result is that the electrodes serve to clean up or purify the gas. Impurities liberated from the walls of the bulb or other parts of the discharge device are also cleaned up and high gas purity results when such material is used for the electrodes.

X-RAY EMISSION SPECTRA OF URANIUM

Siegbahn, 1931 $\lambda = \text{cm} \times 10^{-11}$

K SERIES: $\alpha_1(126.40)$; $\alpha_2(130.95)$; $\alpha_{13}(111.87)$; $\beta_2(108.42)$

M SERIES: $\gamma(3473)$; $\beta(3708)$; $\alpha_1(3902)$; $\alpha_2(3916)$

L SERIES: $\iota(1064.9)$; $\eta(803.5)$; $\alpha_1(908.74)$; $\alpha_2(920.62)$;
 $\beta_1(718.51)$; $\beta_2(753.07)$; $\beta_3(708.79)$; $\beta_4(746.4)$;
 $\beta_6(786.79)$; $\beta_7(734.6)$; $\gamma_1(613.59)$; $\gamma_2(603.86)$;
 $\gamma_3(597.11)$; $\gamma_4(573.6)$; $\gamma_5(634.2)$; $\gamma_8(600.0)$

The breakdown potential of devices using uranium therefore remains remarkably constant as long as the discharge current is not allowed to attain a value so that the inert gas is actually driven into the electrodes, thus changing the gas pressure. Glow rectifiers and low voltage regulator tubes have been constructed with uranium electrodes which showed practically the same discharge characteristics over a period of 20,000 hours continuous operation.

Uranium readily alloys with other metals (Marden and

Rentschler, 1923). It has been alloyed with the following elements: copper, zinc, magnesium, mercury (cf. data on solubility and on Russel's studies on mercury surfaces) aluminum, titanium, vanadium, molybdenum, tungsten, manganese, iron, and cobalt. Usually aluminothermic reduction is used for the preparation of these. Ternary U-Fe-Mn has been prepared and a quaternary, U-Mo-Cr-Ti, was prepared by A. Stavenhagen and E. Schuchard in 1902. Intermetallic compounds have been prepared with antimony and arsenic. The Theory of Arranged Mixed Phases studied by C. Wagner and W. Schottky (1930) included the U-O system.

Production of a new binary alloy of uranium and nickel, containing 66% uranium, is useful in that it is highly resistant to corrosion, being attacked with difficulty even by aqua regia. This alloy has a low melting point and is quite miscible with molten steel, nickel, or copper. Another alloy of uranium is that with copper and contains up to 20% ura-

URANIUM LINES

Exner and Haschek

ARC			
λ	I	λ	I
3932.19.....	1	5493.15.....	10
4090.26.....	5	5528.01.....	10
4171.74.....	5	5915.61.....	8
4341.83.....	5	6395.68.....	8
4355.82.....	5	6449.38.....	10
SPARK			
λ	I	λ	I
4090.28.....	4	4545.76.....	4
4241.88.....	4	4555.30.....	4
4269.84.....	4	4603.86.....	4
4341.89.....	4	4627.26.....	5
4355.89.....	4	4646.80.....	4
4472.55.....	6	4689.28.....	4
4515.50.....	4	5493.16.....	4
4543.79.....	7	5528.02.....	4

nium. Its desirable properties are those of high conductivity and resistance to corrosion. The probability of an assured supply of uranium may lead to important outlets in the metallurgical field.

As has been previously mentioned uranium in the finely divided state is pyrophoric. When prepared properly the grey or black powder vigorously unites with the oxygen in the air to form its oxide. Pyrophoric uranium may be obtained by reduction of the oxide with magnesium in the Goldschmidt Reaction. Alloys of Fe-U with more than 20% uranium are pyrophoric and it appears that the activity increases with the uranium content of this binary.

Spectral Characteristics

The various types of *spectra* for uranium have been studied extensively. The determination of uranium by spectrochemical methods in the ordinary sense is, at present, of little value since uranium in amounts less than 7 per cent is easily masked by elements which produce stronger and/or more characteristic spectra. Probably the most apparent reason for this is that the atomic emission for uranium is extremely complex, this fact obviously being associated with the atomic nature of the element. It is noteworthy, however, that spectromicroscopy offers much promise in the study of uranium salts when in the form of small crystals.

The compounds of uranium generally do not color a non-luminous flame and, as has been pointed out, the emission spectra of uranium salts is so rich in lines, which are not in any manner characteristic of the element, so as to be practically valueless. Spark spectra for uranium were first studied by R. Thalen, G. Meyer, and others. Important investigations were made on spark and arc spectra by Exner and Haschek in 1911. These investigators also determined the intensity (I) of the major lines (see table). It will be noted

that those lines which have the greatest intensity are not necessarily those which are most persistent.

In 1909 Pollak made important investigations on the spark spectra of solutions of uranium chloride to determine the most persistent lines. The results are shown in the table. Wave lengths are in Angstrom Units and intensity is denoted by I , while the persistence (P) of the lines is denoted by:

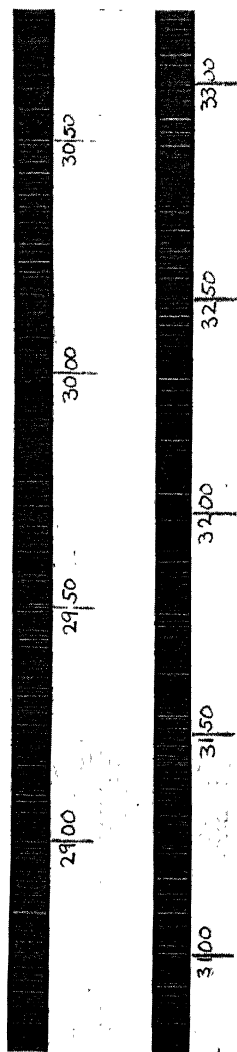
ϕ = Seen with one per cent solutions but not with 0.1 per cent solutions.

χ = Seen with 0.1 per cent solutions but not with 0.01 per cent solutions.

ψ = Seen with 0.01 per cent solutions but not with 0.001 per cent solutions.

POLLAK'S TABLE OF THE SPECTRAL LINES FOR URANIUM

$\lambda = A.U.$	I	P	$\lambda = A.U.$	I	P
4605.4.....	4.....	ϕ	3244.4.....	2.....	ϕ
4603.9.....	ϕ	3093.1.....	2.....	χ
4543.8.....	7.....	ϕ	3072.9.....	2.....	ϕ
4415.4.....	2.....	ϕ	3058.0.....	2.....	χ
4371.9.....	2.....	ϕ	3044.3.....	2.....	χ
4355.8.....	4.....	ϕ	3006.9.....	1.....	ϕ
4341.9.....	4.....	ϕ	2974.2.....	1.....	ϕ
4241.9.....	4.....	ψ	2971.2.....	2.....	ϕ
4171.8.....	3.....	ϕ	2969.6.....	1.....	ϕ
4090.3.....	4.....	χ	2941.9.....	2.....	χ
3979.9.....	2.....	ϕ	2888.3.....	1.....	ϕ
3954.9.....	2.....	χ	2865.7.....	2.....	χ
3874.2.....	2.....	ϕ	2828.1.....	1.....	ϕ
3859.7.....	2.....	ϕ	2794.0.....	2.....	ϕ
3883.0.....	2.....	ϕ	2790.8.....	1.....	ϕ
3693.9.....	2.....	χ	2766.0.....	1.....	ϕ
3672.7.....	2.....	ψ	2742.7.....	1.....	ϕ
3552.4.....	2.....	ψ	2733.4.....	1.....	ϕ
3453.7.....	2.....	ϕ	2635.6.....	1.....	ϕ
3436.9.....	2.....	ϕ	2552.5.....	2.....	χ
3337.9.....	2.....	χ	2549.5.....	1.....	ϕ



A portion of the ultraviolet spectrum of uranium, illustrating the complexity of the emission of this element. Only about five per cent of the entire range that can be recorded photographically is shown. This is typical of the whole, which consists of many thousands of fine lines and which demonstrates the impracticability of direct spectrochemical analysis of uranium. (Spectrogram by Dr. W. F. Meggers, National Bureau of Standards)

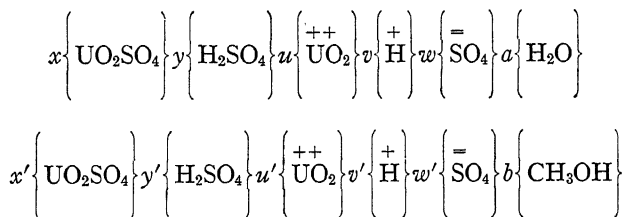
Uranium sparks under water have characteristics not peculiar to sparks produced in gaseous atmospheres. Allin (1927) found that the uranium spark under water gives a perfectly continuous spectrum with neither absorption nor emission lines. According to van Heel uranium is the only element other than the rare earths, whose compounds exhibit line absorption spectra.

Harry C. Jones, et al, conducted extensive researches on the absorption spectra of solutions of comparatively rare salts. One of the first of these investigations was in 1910 and concerned uranium. A number of important facts were revealed in the studies, e.g., the uranyl spectrum consists of about twelve bands beginning at 5000 A.U. and extending into the ultraviolet region.

The bands themselves form a series, the distance between these decreasing with the decrease in wavelength. On the other hand, uranous bands do not form any series yet they resemble the uranyl bands in their general appearance. The difference between the two sets of bands was shown by the absorption spectrum of a uranous salt during slow oxidation to the uranyl salt by oxygen.

Jones and Strong (1916) regarded the *modus operandi* by which uranyl salts are transformed into uranous and vice versa as not being known with certainty. It appears likely that there is not the usual dynamic equilibrium which ordinarily exists between uranyl salts and uranous salts.

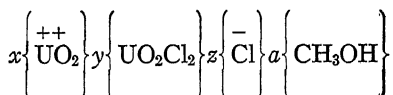
Jones and his co-workers emphasized the importance of aggregates. Aggregates, being very complex molecular clusters, have been assumed to be the centers of light emission and also where dissociation and recombination effects occur. Jones and Strong gave a typical example of an aggregate consisting of two different compounds dissolved in a mixture of two different solvents:



where it is assumed that at the usual concentrations, u , w , u' , v' , and w' have small values. The significant aspect of these studies is that absorption centers are aggregates of definite composition and that all the coefficients in the equation have a definite value.

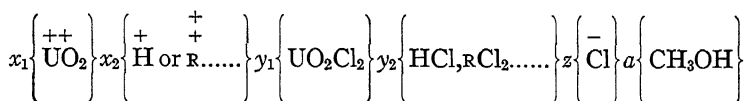
The Theory of Aggregates assumes further importance by explaining a number of actions which occur in the chemistry of the uranium compounds and which may be unrelated to absorption spectrometry. For example, compare the Theory of Aggregates with actions that occur in uranium beads and other solid solutions (phosphors).

The same investigators also studied the effect of change in temperature on the intensity of *solvate bands* from uranium solutions. A striking effect was noted on the absorption spectra of uranous halides with water and alcohol as solvents. It was found that solvate bands appeared as a result of aggregates which had been formed. These aggregates exerted an influence so as to alter the character of the absorption spectrum of uranium solutions. The aggregate formed with uranyl chloride in methanol, according to Jones and Strong, may be represented as:



In this system, and in most other cases, x , x' , z , and z' may be small; y and y' may also be small, but if hydrochloric acid

or other chloride (of R) is present, the system may have the following structure:



Fluorescence and Color

The fluorescence of uranium compounds was first studied by Sir G. G. Stokes in 1852. Later the pioneer in the field was Becquerel who in 1872 made extensive investigations on the spectral nature of the fluorescent light emitted by uranium compounds. A year later Morton and Bolton studied some 85 uranium salts but it really remained until 1912, and on, for Nichols, Howes, Merritt, Wilber, and Wick in a series of classic researches to reveal a large number of new facts concerning the fluorescence spectra of uranyl compounds. Their investigations were summed in papers published by the Carnegie Institution of Washington but many significant details yet remain for practical application.

Nichols, et al, found that the changes which occur when the temperature of uranyl salts is slowly changed from +20° C. to -180° C. include:

- (1) An increase in intensity of the entire spectrum. —
- (2) A shift which is more often toward the violet than toward the red, although both shifts may occur between the above temperatures.
- (3) A narrowing of the bands and oftentimes a resolution of the bands.
- (4) A slight alteration in frequency interval.
- (5) The formation of one or more definite hydrates (cf. data on aggregates by Jones and Strong).

(6) A change in the form of the bands.

The changes produced by dilution include:

(1) A shift in the entire spectrum.

(2) A change of interval.

(3) A change in the hydrate.

(4) A decrease in resolution except when the equilibrium is altered by the addition of small amounts of acid.

(5) A decrease in intensity.

These investigators obtained other important details concerning the fluorescence spectra of uranyl salts. They found that the fluorescence spectrum of uranyl sulfates consists of eight equidistant bands, the first and eighth of which disappear at the temperature of liquid air. The remaining bands are resolved into groups of narrow line-like bands, the homologous members of which form a series having constant frequency intervals ranging from 85.7 in cesium uranyl sulfate to 83.0 in potassium uranyl sulfate.

The fluorescence groups were found to be distinguished by a strong pair of bands about eight frequency units apart and seven weak bands, some of which are doublets.

In the uranyl sulfates there is a general shift of all bands toward the violet, with increasing molecular weights, of about fifteen frequency units in passing from the spectrum of uranyl sulfate to that of cesium uranyl sulfate. The absorption spectra of the sulfates are made up of a series of bands having a frequency interval with a general average of 70.3.

These absorption series extend into group seven of the fluorescence without a break of interval. There are many reversals where fluorescence bands and absorption bands overlap. The reversing region is therefore one group further toward the red than in most spectra of the uranyl compounds.

The spectra of the uranyl acetates consist of the usual

equidistant bands. With excitation at liquid air temperatures the bands are resolved into groups, the homologous members of which form a series of constant frequency intervals. In two single acetates, an anhydrous variety, and a crystalline form with two molecules of water of crystallization the spectra differ widely, particularly as to the groups of fluorescence bands.

In the double acetates, those containing Li, K, Ca, Mn, and Sr, the spectra are essentially identical both as regards the location of the principal bands and the structure of the fluorescence groups. The only distinctions between their spectra are in the sharpness of resolution and relative brightness of the components. In the spectrum of barium uranyl acetate the groups are shifted about five frequency units toward the red. In the spectra of the double acetates of ammonium and rubidium, band D in each group is doubled without a shift in groups.

The presence of Na, Mg, Zn, Ag, and Pb modifies the group structure by the addition of bands characteristic of the metal and causes slight relative displacements of the group system as a whole. The frequency interval for the fluorescence series of the double acetates is probably the same for all series and for all salts, the departures from the general averages for the various salts being less than one frequency unit from the general average, i.e., 84.76. The same is probably true of the absorption series, the general average for which is 70.68. The frequency intervals, both in the fluorescence and absorption spectra, are larger by more than one frequency unit for the single acetates than for the double acetates.

Nichols, et al, found that in uranyl salts in solid solution, as in canary glass or in fluoride beads, the banded fluorescence spectrum with constant frequency intervals, as observed at $+20^{\circ}\text{C.}$, is not further resolved into groups of

narrow line-like bands by cooling to the temperatures of liquid air. This should be compared to the section in the chapter on analysis in which bead tests are treated.

Crystalline sodium uranyl phosphate and ammonium uranyl phosphate fluoresce at low temperatures in bands which are fully resolvable. Of interest in uranometry is that the presence of an excess of phosphoric acid, with the above compounds or uranyl phosphate in solid solution of vitreous structure, resolution does not occur on cooling (cf. Theory of Aggregates).

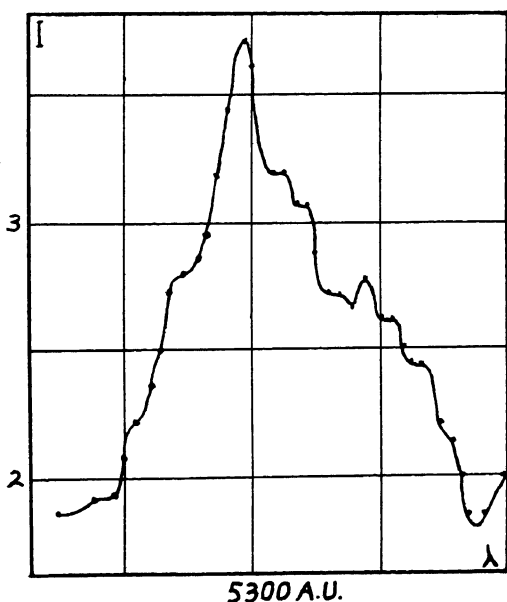
Polarization occurs in the fluorescence and absorption spectra of the four double chlorides $[R_2(UCl_6)]$ where R may be NH_4 , K, Rb, or Cs, all these crystallizing in the triclinic system. The spectra differ from the other compounds examined in that both in the fluorescence and absorption regions each band is resolved at $+20^\circ C.$ into a group of five bands forming homologous series of constant frequency interval.

The structure of the fluorescence spectrum is essentially the same in the different salts, the spacing of the bands of each group repeating itself in the successive groups, excepting in the reversing region where the appearance is modified by the overlapping of fluorescence and absorption bands. Each of the five bands in a group constitute a doublet, the two components of which are polarized at right angles to one another. The frequency interval probably is the same for each series in a given salt.

In the double chlorides the position in the spectrum of a given band varies slightly but systematically with the molecular weight of the salt. The order of diminishing wavelengths was found as: K, NH_4 , Rb, Cs; the shift from K to Cs being of the order of five Angstrom Units. This shift is in the same direction, from red toward violet, for all the homologous series and of the same size within the errors of

observation. Cooling to the temperature of liquid air produces the usual narrowing of bands, apparent shifts of position, and apparent changes of interval, all of which changes are explained by the relative enhancement or diminution of components of the bands.

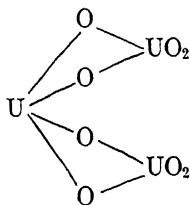
As is well known eye-interpretation of light is not necessarily identical with the interpretation by an instrument, e.g., spectrophotometer or uncorrected photocell, whose "perception" and/or "visual acuity" differs considerably from the human optic apparatus. Although the preceeding data may be regarded as a basis for most interpretations of color by the eye the same data may serve further to explain the colors of uranium compounds.



Illustrating characteristic color and fluorescence of uranium salts. The location of crests with uranium as an activator in fused beads of sodium fluoride is shown.

The colors of the compounds of uranium are generally green, red, yellow, orange, and black. The greater part of those compounds which contain the uranyl radical (UO_2) appears to be characterized by a green or lemon-yellow color. This holds very closely for the fluorescence of uranyl compounds (re. studies of Nichols, et al.). According to Dake and De Ment (1941) practically all fluorescent uranium minerals emit the larger part of light in the yellow and green regions irrespective of exciting wavelengths. Intense fluorescence does not appear to be recognized for longer wavelengths, e.g., red or orange. A vivid yellow or yellow-green luminescence has been observed in most studies on the uranium salts by numerous other investigators, e.g., Radley and Grant summarized these in 1933.

As regards the correlation of structure and composition of the various uranium salts with color several interesting aspects may be noted. Uranous salts, the oxide of which is exemplified by UO_2 are green while uranic salts, the oxide of which is exemplified by UO_3 are yellow. Yellow-green fluorescence and lemon-yellow colors found in a number of uranium compounds may be interpreted on the basis of both these forms of uranium, e.g., urano-uranic oxide:



In this case the UO_2 radical presumably may be regarded as the cause of the green portion of the color, in effect a green-producing chromophore, while the remainder might be regarded as the causative factor for the greater portion of

the yellow color also in effect a yellow-producing chromophore.

Uranium as an Activator

An activator or phosphorogen is a trace of material, usually a metallic element or ion, whose presence is necessary for the fluorescence of many minerals and substances which can otherwise be termed solid solutions. Uranium plays a peculiar role by its fluorescence activation. While uranium is naturally radioactive, investigations have not shown this to hold any striking correlation with its fluorescence activating properties. Uranium as an activator has been established in opal, as well as in certain agates and glasses. Hyalite opal and common opal from Mexico, North Carolina, Wyoming, and Nevada, fluoresces an intense greenish-yellow, presumably due to the presence of minute amounts of uranium.

H. C. Dake, John D. Buddhue, and others, have been instrumental in revealing important information about the activating action of uranium in minerals. The moss agate from Sweetwater County, Wyoming fluoresces a color and intensity characteristic of the secondary uraninites. Large masses of colorless chalcedony found elsewhere in Wyoming have a green-yellow fluorescence similar to the agates from Sweetwater. Agatized wood and agate casts of wood from the same vicinity fluoresce similarly, but not as intensely. The effects of concentration on fluorescence, as well as the nature of the base, probably explain this. Milky quartz, quartzite, and dark jasper also fluoresce with this green color. More recently other agate producing localities have been found in Wyoming and often this material fluoresces a green color. The localities are one-hundred miles apart but are all on the same general geological horizon. The rocks and sedimentary formations of central Wyoming, including

Sweetwater County, are known to be radioactive to an abnormal degree.

In specimens of fluorescent Wyoming moss agate, inclusions of a canary yellow mineral have provided the basis for studies. The inclusion in one specimen was about six millimeters under the surface and fluoresces intensely under both short and long wavelength ultraviolet radiation. The greenish-yellow fluorescence was identical to that of most secondary uraninites. The inclusion was found radioactive by its effect on a photographic plate.

Spectroscopic examination of Wyoming agate by J. D. Buddhue (1939) failed to definitely establish the presence of uranium. However, in view of other evidence and the sensitivity of spectroscopic methods (see the chapter on analysis by spectrochemical means) tests of greater delicacy were performed on the same specimen. A chemical examination by T. Kennard showed uranium in amounts greater than a few parts per million. Further studies by Buddhue on fluorescent chalcedony from the same locality by fluorescence spectroscopic methods definitely excluded autunite as the activating substance since bands obtained did not coincide with those of autunite.

The presence of phosphorus, which would have indicated autunite or chalcilite since both are phosphates, was not demonstrated either. However, Buddhue is of the opinion that the fluorescence of Wyoming agates and chalcedony is due to an unidentifiable compound of uranium. This is apparently present in small amounts and probably contains the uranyl radical and may be a new mineral species since its fluorescence spectrum appears to be unlike that of uranium compounds studied. Since vanadium was found to the extent of 0.1% it might be possible that ferghanite, hydrated uranyl vanadate, is the cause as its color, sulfur yellow, is about

the same color as the inclusion noted in the Wyoming moss agate.

Uranium probably activates the greenish-yellow fluorescence in certain specimens of water. It is noteworthy that fluorescence, other than whitish or bluish, in water is not common. The studies of Francesconi and Brund in 1934 attributed the greenish-yellow fluorescence in certain waters to the presence of radioactive elements. It is probable that uranium was the activating agent in these instances.

H. C. Dake in 1937 studied the fluorescence of the water of Lost Creek and Lost Lake, north of Wamsutter, Wyoming. Lost Creek cuts through the deposits of the secondary uraninite mineral schroeckeringite (dakeite), and leaches out the water-soluble mineral. The creek water above the deposits failed to show the characteristic greenish-yellow fluorescence, while below the deposits the water was distinctly fluorescent. The water of Lost Lake was only feebly fluorescent, probably due to dilution of the uranium salts.

Uranium in the Colloidal State

The accounts of the colloid-chemistry of uranium in the literature are scanty. Unstable sols were first prepared by Graham in 1861 and later by Aloy in 1899. Svedberg (1909) prepared the isobutyl alcosol of elemental uranium by using an oscillating electric arc. This organosol was stable for only 12 hours and was brownish-black by transmitted light and black by reflected light.

The hydrous uranium dioxide sol was first prepared by Aloy. He obtained a voluminous red-brown mass by adding an alkali to a uranous solution. Weiser regards it as probable that the mass would be peptized by washing since Samsonow (1911) obtained a sol by washing the dark hydrous dioxide precipitated during electrolytic reduction of

fifty grams of uranyl chloride in one hundred cc. of 2 N. HCl. This sol, when freshly prepared, contained small positively charged particles in rapid Brownian movement. These particles grew rapidly and within 24 hours most of the oxide settled out.

The sol of hydrated uranium trioxide hydrate was first prepared by Graham in 1861. He added potassium carbonate to a uranyl salt which contained sugar and dialyzed the mixture. The deep orange-yellow colloid was very stable but was readily agglomerated by electrolytes. The same sol was prepared by Szilard in 1907 without the use of sugar. To obtain the oxide in a suitable form Szilard mixed a solution of uranyl acetate with ether and exposed this solution to light thereby producing a violet hydrous precipitate which had been shown by Aloy in 1907 to be U_3O_8 .

Weiser (1935) regarded it probable that the sol is a hydrate rather than a hydrous oxide since the anhydrous oxide takes water at room temperature, this being shown by Lebeau in 1912. A dihydrate is formed as a result of this, which on heating (at 80° C. and at water-vapor pressure of 15 mm., shown by Huttig and Schroeder in 1922) reverts to the monohydrate.

Some significance of uranium sols lies in analyses which involve colorimetry or nephelometry. The ferrocyanide test, sometimes used to estimate uranium, is often in the form of a relatively stable sol. The effect of various salts on this sol was studied by N. P. Chatterjee in 1930. He found that the concentrations of salts, in gram-atoms, required to coagulate a very stable uranium ferrocyanide sol (deep brown in color) follow a definite series:



The addition of potassium ferrocyanide as a protective colloid was also found to increase the coagulation concentra-

tion. The determination of sol changes the coagulation concentrations by changing potassium and ferrocyanide concentrations in the micellar liquid (cf. the ferrocyanide test for uranium in the chapter on analysis).

Another little referred-to fact in the colloid-chemistry of uranium is its use as a colorant in the ceramic industries. The various uranium compounds used to color glazes have been regarded as probably present as colloidal suspensions (suspensoids), this having been pointed out by many investigators, e.g., C. W. Parmelee, 1929.

The compounds of uranium which are of chief interest to the glaze maker are mainly the oxides. Probably the most important is U_3O_8 , the green oxide of uranium. The "black oxide of uranium," U_2O_5 , is also used for this purpose. Other compounds which are used by the ceramist are: sodium diuranate ($Na_2U_2O_7$) or "uranium yellow"; a similar potassium salt; ammonium uranate which is also known as "uranium yellow"; the hydrated sodium uranate ($Na_2U_2O_7 \cdot 6H_2O$), the third uranium compound which is called "uranium yellow." In Germany a hydrated sodium uranate (*urangelb*) is available for use as a coloring agent in glasses and differing from the first sodium uranate by having three less water molecules. In addition to the use of oxides other compounds such as the double salt, sodium uranyl carbonate, and the nitrate and sulfate, have been suggested.

Related to uses as a colorant in ceramics is the use of uranium for coloring glass. The element is not a powerful colorant, as compared with elements such as chromium or cobalt, but deep colors may be obtained when larger proportions of the substance are incorporated in the batch of glass. The uranium glasses are unique in themselves since they are highly fluorescent in ultraviolet radiations of all wave lengths as well as in white light. The fluorescence is so intense in bright white light that the glass appears self-luminous.

Solubility in Alteration and Age-Determination

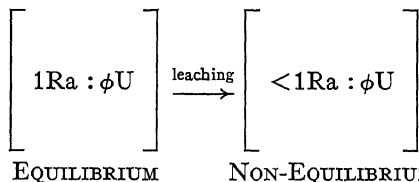
The solubilities of uranium, radium, and thorium compounds are of much more significance than would first appear. From a mineralogical standpoint the solubility of uranium compounds is important from a two-fold aspect. Assuming that at least partial conversion of primary uranium minerals, e.g., uranium oxides, occurs by action of solutions to form secondary uraninites, solubility is important.

The other aspect is illustrated by the studies of I. Starik in 1936. These investigations concerned the leaching-out of uranium and radium. It was found that radium is more readily extracted by melts, weakly acid, or weakly alkaline media, than uranium. This fact is important in determinations of the age of radioactive minerals, a typical relationship for this being the formula of Holmes and Lawson:

$$T = \left(\frac{\text{Pb}}{\text{U} + 0.38 \text{Th}} \cdot 7400 \right) \left(1 - \frac{x_1}{2} + \frac{x_2}{3} \right)$$

with $x = 1.155 \left(\frac{\text{Pb}}{\text{U} + 0.38 \text{Th}} \right)$ and as is well known such formulae a number of which are known, are generally based on the ratio which exists between radium and uranium according to Boltwood's Constant. According to this constant one part of radium maintains an equilibrium with 3.4×10^6 parts of uranium.

Should leaching-out of radium occur by melts or other mechanisms from uranium minerals the equilibrium would be disrupted:



with Boltwood's Constant being represented by ϕ .

In studies by Starik it was assumed that radium is not present in the crystal lattice of the mineral but present in the capillaries. Uranium is, on the other hand, in the crystalline lattice and therefore the migration of uranium is greatly retarded since it can only occur with solutions of uraniferous minerals.

Of additional interest is the solubility of uranium, radium, and thorium salts. This is true especially for those salts which occur naturally, i.e., as minerals. It has been pointed out (studies adopted from the investigations of Miexner and others) that uranium micas and other silicates are relatively insoluble, this fact being associated with the existence of primary uranium minerals.

Moreover, uranium minerals which exist in nature like the double arsenates, phosphates, carbonates, and others are all relatively soluble. Radium salts of this sort are all generally soluble with the exceptions being the sulfate and hydroxide. It might follow, therefore, that leaching-out of either or both of these elements would be a function, at least in a partial sense, of their solubility. This would mean that the nature of the compound(s), as well as the nature of the solute(s), would be of appreciable importance in radioactive equilibrium. Data on the solubility of such salts is given in the accompanying table.

Once in solution uranium, is more readily held in solution than the others, especially radium. In secondary radioactive minerals the equilibrium is disturbed because of the migration of radium, a fact of greatest pertinence to the determination of geologic age of minerals.

Correlated to leaching-out and solubility of these elements are the studies of G. Kirsch and F. Hecht in 1938. These investigators found that uranium concentrates in the acidic differentiates with the result that caution must be exercised in determining geologic age of minerals on the basis of their uranium, radium, and/or thorium contents.

WATER-SOLUBILITY OF GEOLOGICALLY IMPORTANT RADIOELEMENT SALTS

	<i>Uranium</i> (UO_2^{++})	<i>Radium</i> (Ra^{++})	<i>Thorium</i> (Th^{4+})
Oxide.....	—	—	Insoluble
Sulfate.....	Soluble.....	Insoluble.....	Soluble
Silicate.....	Insoluble.....	Soluble.....	Insoluble
Hydroxide.....	Insoluble.....	Insoluble.....	Insoluble
Carbonate.....	Soluble.....	Insoluble.....	Soluble
Phosphate.....	Soluble.....	Soluble.....	Insoluble
Arsenate.....	Soluble.....	Soluble.....	Soluble

Biophysical Aspects: Radiation Injury

The rapid increase in the use of artificially radioactive substances and the greater availability of exceedingly powerful sources of subatomic particles, especially neutrons, directs attention to the dangers present in this work. The unfortunate state which existed after the discovery of X-rays and radium serves to warn of the precautions to be taken in the face of these new and much more injurious agents.

Neutrons appear imminently to be of most danger. These extremely penetrant particles produce their effects on living cells and tissues by the secondary recoil rays formed in an organism collision with hydrogen, carbon, nitrogen, oxygen, or other atoms which may comprise the structure of living tissue.

Robley D. Evans, one of the foremost in the field of radiation protection, has compared the effect of neutrons to alpha rays from radium. Alpha rays from radium are more closely like the recoil effect of neutrons than other radiations which have so far been studied extensively with regard to their effects on living tissues.

According to Evans, as little as one-hundredth of an "n" per day of fast neutrons may be unsafe if the exposure con-

tinues for over a period of about ten years. The unit used to measure neutron dosage, the n-unit, parallels that used in X-ray dosage, the r-unit.

While neutrons have been used for about eight years or so the question of the effects of small doses of these particles over a long period of time arises as being more obscure than the same question applied to the particles emitted by radium. It is admitted that the effects of particles in very small dosages over a long period of time are practically unknown. Animals can only be used to a certain extent in this investigation since their susceptibility and tolerance varies considerably; much evidence is lacking which might otherwise simulate and re-enforce, but not be identical with, studies on humans.

The tremendous destructive power of alpha particles, under proper conditions, is not ordinarily realized. Alpha particles, while not penetrating matter to a very great degree, were directly the cause of death in the girls who, sometime ago, ingested radioactive luminous paint containing from 10 to 180 micrograms of radium. In these cases death generally resulted but was preceded by anemia, sarcoma, and emaciation. The number of alpha particles emitted by radium, for example, is fully a million times the number emitted by an equal amount of uranium.

The effects of radon may be ascribed to alpha particles. The qualitative effects of these radiations have been found to be similar to those of beta, gamma, and X-rays. It is known that alpha particles, when emitted in the mammalian body at relatively low rates over considerable periods of time, produce serious pathological conditions, including malignant growth. The precautions to be observed for neutrons should be stimulated by information of this sort.

The generally used protective measure for neutrons is a wall of water. Protection from neutrons is obtained by those

who work with the University of California cyclotron by cans of water several feet or more thick, behind which the operators stand.

Artificially radioactive elements are quite often beta emitting. The usual precautions taken against beta rays include lead sheets several millimeters or more in thickness. The strength of the preparation governs, of course, the thickness of the lead placed between the operator and the active material.

Gamma rays, on the other hand, are highly penetrant. They are not entirely absorbed by several centimeters of lead; and, sheets used to screen-out beta and gamma rays should be constructed with a considerable safety factor. The National Bureau of Standards has issued a small handbook (H23) on *radium* protection. In this the proper lead thicknesses advised for protection from radium preparations of various strengths are described.

Consider that as little as one-millionth of a gram (one gamma) of radium will deposit in the bones within eight hours after ingestion and can result in death in from eight to twelve years. The highly radiotoxic nature of radium characterizes many of the radioactive elements which are being handled at present.

The most important point is for the worker with radioactive substances to have an ever-present realization of the danger and to carry out all manipulations in such a way as to reduce the exposure to a minimum. Injuries by radioactive substances are insidious and may not become visible until a long time after they have occurred.

5

THE CHEMISTRY OF URANIUM

The Approach by Nuclear Fission

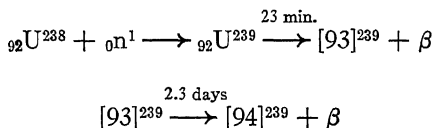
THE importance of uranium has been greatly enhanced by its association with radium. But of still greater promise is the singular use of uranium in an entirely new entity—*nuclear fission*. Likely of ever increasing importance uranium has already been pointed out by the popularizers of science as a fuel of the future. The revived interest in uranium, heretofore a relatively obscure element, has been due to a chain of discoveries, the course of which is of engaging candour bordering on the incredible.

A brief résumé given by Lawrence S. Foster summarized developments to early in 1941. Shortly after the discovery of the neutron by Chadwick, after its prediction by Rutherford, and artificial radioactivity by M. and Mme. Joliot-Curie in 1934, Fermi and his co-workers (1934) demonstrated that heavy elements such as uranium and thorium are capable of capturing neutrons and thereby becoming highly radioactive.

This activity was found not to be associated with the transmutation of the target element into any of the elements between lead with an atomic number of 82 and uranium with an atomic number of 92. Fermi, et al, reached the startling conclusion that transuranic elements—those with atomic numbers 93, 94, and so on—had been synthesized. This interpretation was generally held to be correct until January, 1939, when Hahn and Strassman demonstrated the presence of elements of about half the atomic weight of uranium among the products of such bombardments. These

observations of the *fission* of the heaviest elements were confirmed almost immediately.

Accordingly, the existence of Fermi's transuranic elements was open to serious question. On June 7, 1940, however, E. M. McMillan of the University of California, and P. H. Abelson of the Carnegie Institution of Washington announced that elements 93 and 94 actually can be synthesized. But instead of having properties which characterize eka-rhenium and eka-osmium, their chemical properties appear to correspond more closely to those of uranium itself, thus opening the possibility, that as a consequence of inner-shell building of a new series of elements analogous to but chemically dissimilar to, the rare earths (atomic numbers 57 to 71). This new series makes its appearance with element 93 as the first member. The series of transformation reactions is evidently:



No alpha or beta ray activity or evidence of nuclear fission was detected which could be associated with the decay of $[94]^{239}$. This transuranic element seems to be quite long lived. Except for amplification in details, this phase of induced radioactivity in ${}_{92}\text{U}^{238}$ by bombardment with both fast and slow neutrons seems to have been cleared up.

Even more striking is the explanation of the origin of the elements of low atomic weight. It was noted that two atomic products of fission were ejected in opposite directions at extremely high velocities, thus carrying enormous quantities of energy. Because of their low kinetic energies, particles of ${}_{92}\text{U}^{239}$ and $[93]^{239}$ remain in the layers of target material where they are produced, but the products of fission escape

with such violence that they may be caught a few centimeters from the target and examined chemically. The energies are of the magnitude of 200 Mev. or 4.6×10^{12} calories per gram atomic weight of uranium. It is this tremendous quantity of energy emitted that has given hope that nuclear fission may be the source of atomic power. The energies released in fission of uranium are fully 40,000,000 times greater than those released by one molecule of T.N.T. in exploding.

In April 1940 Nier of the University of Minnesota and Booth, Dunning and Grosse of Columbia University announced that sub-microscopic quantities of the natural isotopes of uranium, U234, U235, and U238, had been separated by means of the mass spectrograph and subjected individually to neutron bombardment.

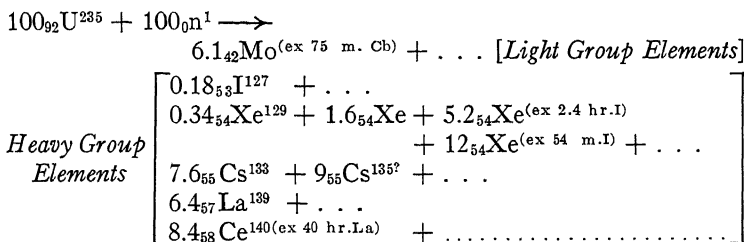
It was found that only the medium-mass isotope, uranium 235, undergoes fission with "thermal neutrons"; uranium of mass 238 is also capable of absorbing thermal neutrons but is transmuted into element [93]²³⁹ just as with more energetic neutrons. The exact sequence of events after the capture of a slow neutron by ${}_{92}\text{U}^{235}$ is still not known, with certainty, but fission is accompanied by the escape of many more fast neutrons than were captured, which makes possible the initiating of a chain reaction. This can occur only in the presence of nonabsorbing objects such as water which reduce the kinetic energy of the secondary neutrons to thermal equilibrium values.

The complex particle, formed by the capture of a thermal neutron by ${}_{92}\text{U}^{235}$, bursts in 10^{-12} second into at least two atomic particles, the nature of which remains uncertain because of their short half-lives. The process of fission is highly complex but in addition to the fast neutrons being ejected, along with energy, two groups of isotopes are formed in the disintegrations of atomic species resulting from fission. The two classes of elements are known as the heavy group

and the light group. In the heavy group atomic weights are between 125 and 150. In the light group atomic weights range between 80 and 100. The reaction has been given by A. Grosse (for up to 1941) to explain fission as shown in the accompanying diagram.

FISSION OF URANIUM 235

Modified, after Grosse



If the atomic weight of individual isotopes is unknown the element is characterized, in the equation, by the half-life of its parent. The equation shows that for the fission of every 100 uranium 235 atoms there will be produced 100 atoms of the heavy group and at the same time 100 atoms of the light group. In addition to these neutrons and enormous quantities of energy are emitted. This indicates that the discovery of added fission fragments is to be expected. Other elements which have been detected in the disintegration of atomic species resulting from fission are: $_{35}\text{Br}$, $_{36}\text{K}$, $_{37}\text{Rb}$, $_{38}\text{Sr}$, $_{39}\text{Y}$, $_{40}\text{Zr}$, $_{41}\text{Cb}$, $_{43}\text{Ma}$, $_{51}\text{Sb}$, $_{52}\text{Te}$, and $_{56}\text{Ba}$.

Isolation and Preparation of Metallic Uranium

In August 1786 M. H. Klaproth showed that pitchblende partly dissolved in aqua regia. When a clear cold solution of pitchblende was added to an alkali an unknown yellow oxide formed. The addition of sulfuric acid, in turn, produced a

lemon-yellow sulfate. Likewise, a green nitrate was formed on reaction with nitric acid and so on.

Klaproth showed that the unknown material was not chromium, zinc, iron, or tungsten, but was an entirely new element. He named this new substance *uranium* in honor of Herschel's then recent discovery of the planet Uranus in 1781. The German and French terms are identical with that of English—uranium. In 1809 J. G. Leonhardi suggested that the new element be called Klaprothium in honor of its discoverer, but unfortunately this did not receive universal acceptance and the original name remained.

After Klaproth's discovery other investigators immediately confirmed the existence of uranium. In 1791 J. B. Richter published a paper on the new element and in 1805 C. Bucholz studied the substance. Klaproth unsuccessfully attempted to prepare elemental uranium by reduction. Despite this it is very interesting to note that Klaproth termed his element "half-metallic" although actually it was not until about 150 years later that studies on crystalline structure by advanced methods really indicated that uranium is a pseudo-metallic element.

It was not until 56 years after its discovery that pure uranium metal was isolated. In 1842 Peligot showed that Klaproth, instead of having obtained the pure element, had only prepared a lower oxide, the dioxide, when he reduced the yellow oxide by sugar charcoal. Peligot prepared metallic uranium by reduction of uranium chloride with sodium in a glazed porcelain crucible. The sodium was covered with layers of dry potassium chloride and interposed by layers of uranium chloride. The reaction was initiated by heating.

Later, in 1882, Zimmermann used a similar method except that sodium chloride was substituted for the potassium chloride which covered the mixture. Moore (1923) used the same procedure to obtain very pure uranium but he also used

a steel bomb which had been evacuated after the components were introduced into the vessel.

On several occasions Moissan attempted to prepare metallic uranium. In 1893 he prepared a somewhat impure uranium metal by reducing uranium oxide, U_3O_8 , with sugar charcoal in an electric furnace. This preparation contained large amounts of carbon and other impurities. In 1896 he tried to produce uranium metal by electrolysis of the double sodium uranium chloride in an atmosphere of hydrogen using carbon electrodes. The uranium produced by this technique consisted of a spongy mass containing small metallic crystals.

At present the preferred method for preparing uranium metal is electrolysis. In 1901 Ferey electrolyzed a solution of uranium chloride, the metallic uranium being isolated in an amalgam since mercury comprised the cathode of this arrangement. The pure uranium was separated by distillation in a vacuum but the metal obtained was in such a finely divided state that it was pyrophoric, i.e., ignited spontaneously in the air. Such preparations of uranium, however, were free from many of the impurities present in specimens of metal which had been produced by reduction with carbon or other materials.

In 1919 Pierle and Kahlenberg endeavored to substitute non-aqueous solvents for the water solutions of the uranium salt which were previously used. These investigators found that suitable solvents consist of pyridine, amyl alcohol, ether, and ethyl acetate. In solutions of these organic solvents salts of uranium (anhydrous) were electrolyzed. Their results by these methods were somewhat unsatisfactory since only small quantities of uranium metal were obtained.

Undoubtedly the most successful technique for isolating large amounts of pure uranium metal is that of electrolysis of fused salts. This technique was developed by F. H. Driggs and W. C. Lillendahl in 1930. The procedure was to elec-

trolyze, at comparatively low temperatures, mixtures of fused salts. The principal portion of the baths consisted of the halides of the alkali or alkaline earths with a small amount of uranium salt added.

The investigators used several salts in proportions which varied, e.g., sodium chloride, sodium fluoride, potassium chloride, potassium fluoride, and calcium chloride. After fusion of the mixture of these salts one or more of a number of uranium compounds were added in small amounts, e.g., uranium trioxide, potassium uranous fluoride, uranyl chloride, and uranous chloride.

The baths contained uranium trioxide and uranyl chloride as the source for uranium and the principal product obtained on the cathode consisted of black crystals of uranium dioxide. With potassium uranous fluoride or uranous chloride the loosely adhering deposit consisted of metallic uranium or a mixture of the brown oxide which may have been formed from the oxidation of deposited metal.

Driggs and Lilliendahl (1930) stated that the results seem to indicate that uranyl salts are unsatisfactory for electrolytic reduction since they appear to ionize to the uranyl, UO_2^{++} , ion and are deposited upon the cathode as the dioxide. Salts such as those of tetravalent uranium, the chloride, for example, appear to yield the uranous, U^{++} , ion in a fused bath and may be electrolyzed to metallic uranium. The investigators found the most satisfactory procedure to be that consisting of a bath of equal parts sodium chloride and calcium chloride to which was added the green uranium salt KUF_5 .

Uranium buttons and wire have been made from the powdered metal. The powdered uranium is pressed into cylindrical buttons and heated until the metal fuses and separates from the residue. The residue consists mostly of the oxide. It is extremely difficult to determine the metal content of powders because of the occluded gas which they contain and

because of their reactivity. Fused or sintered metals can be easily analyzed.

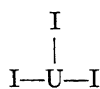
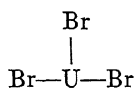
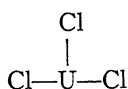
Wire is made from the fused buttons by cold rolling. When about 50% reduction in cross-section occurs, from cold rolling, the wire is annealed for a short time at a temperature of between 900 and 1000° C. The operations are carried out in a vacuum and are performed twice before wire of a suitable nature is obtained. Wire has been rolled to about 0.8 mm. in diameter. Fine wire is prepared by rolling under iron and afterwards dissolving the iron from the uranium by acid.

Valency and Series Ascension

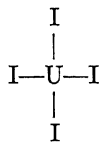
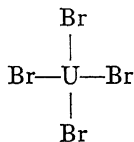
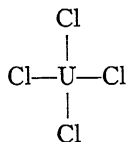
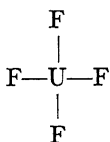
As with a number of other elements, the valency of uranium has long been a source of contention. However, with the greater amount of studies being performed on its compounds, and with the larger number of new compounds being prepared, more definite data on the combining capacity of this element has been revealed. It is definitely established that the lowest valence of uranium is 3, with other valences 4, 5, and 6, also being definitely established. The basis for a lower valence, 2, is not decisive, the information for such an assumption having been obtained from the difluoride, monoxide, and monosulfide of uranium, UF_2 , UO , and US , respectively.

The alleged existence of bivalent uranium appears to have been conclusively disproven by the studies of R. Flatt and W. Hess in 1938. Alibegoff (1886) believed that bivalent uranium existed and attempted to prove this by reduction of uranium disulfide with hydrogen. The former investigators attribute his results to the presence of oxygen in the hydrogen. An octavalent uranium has also been supposed to exist but the evidence was not unequivocal, data being based on the studies of P. Melikoff and L. Pissarjewsky on uranium tetraoxide, UO_4 .

In reality little is known concerning the compounds which involve the lowest valency, trivalency. Trivalency is exemplified by three uranium halides and a hydride, UH_3 :

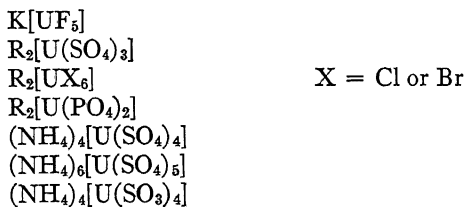


Tetravalent uranium is established by the existence of the following halides:



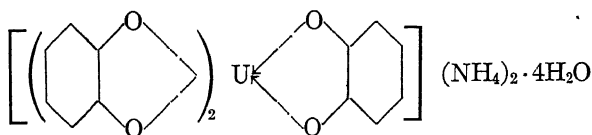
These halides may be conveniently represented by UX_4 where X may be any one of the halogens. Tetravalency was demonstrated by the molecular weight determinations of J. Zimmermann and L. Reigheimer. These investigators also studied the dioxide and the disulfide, UO_2 and US_2 respectively. The tetravalency of uranium was also shown by investigations of W. Hillebrand, who demonstrated the isomorphism of thorium and uranium dioxides. A similar work on the disulfates was done in 1892 by Hillebrand and N. Melville.

A number of double salt types are known:

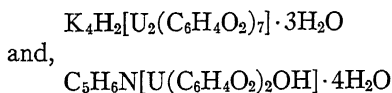


A number of organo-uranium compounds are known which involve tetravalent uranium. One of these is the com-

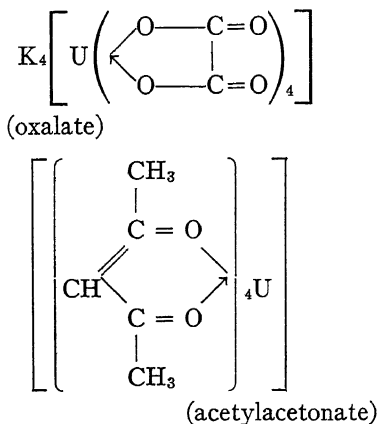
plex obtained by A. Rosenheim, *et al.* The complex involves pyrocatechol:



Other more complex analogs which involve organic addenda are:

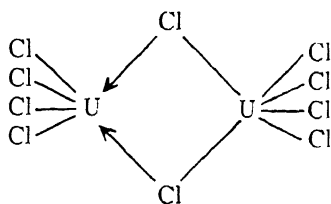


Uranous derivatives containing organic structures are also the oxalate and the acetylacetonate:



When liquid chlorine acts upon the tetrachloride of uranium a pentachloride, UCl_5 , is produced. This may also be formed when uranium is chlorinated. The pentachloride exemplifies *pentavalent* uranium. The pentachloride dissociates at 20°C . although in the corresponding halogen, fluorine, a mixture of tetrafluoride and hexafluoride is pro-

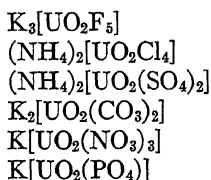
duced. Morgan and Burstall (1936)* suggest the following constitution for uranium pentachloride:



The most stable compounds of uranium are those which are *hexavalent*. The hexavalency of uranium was first decisively established in 1909 by O. Ruff and A. Heinzelman who studied the vapor density of uranium hexafluoride, UF_6 . Since ammoniacal solutions precipitate ammonium uranate, in which the trioxide UO_3 appears as the anhydride of uranic acid, it further indicates that uranium is hexavalent in this oxide as well as in UO_2 (uranyl) derivatives.

Hexavalent uranium compounds, apart from UF_6 , are oxygenated and contain UO_2^{++} which functions as a bivalent acidic radical (cation) such as in uranyl nitrate and uranyl acetate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$, respectively.

The *uranyl radical* is involved in the following coordinated compounds, as well as in a number of others:

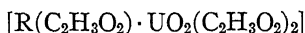


The uranyl radical is also involved in $[\text{UO}_2\text{Cl}_2 \cdot n\text{NH}_3]$

* See Morgan and Burstall, *Modern Inorganic Chemistry*, Chemical Publishing Company, Brooklyn, New York (1936).

where n may equal 6, 4, or 2 (cf. following data by Sutherland on the ammimo derivatives of uranium).

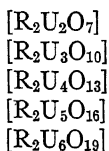
The uranyl group is contained in a number of double acetates which may be represented by:



The best known representatives have $R = Na, Rb, Cs, Tl, NH_4$, or Ag . Needless to say some secondary uraninites may be regarded as analogs to the double acetates, the acetate being replaced by other groups such as carbonate, arsenate, or sulfate. The double acetates provide a basis for the analysis of uranium (see the chapters on uranometry). They separate into long needles or slender tetragonal prisms terminating in pyramids. As would be expected they constitute an isomorphous series.

The sodium salt is the least soluble, a fact of importance in microchemical methods which depend on separation. The ammonium salt is so soluble that in uranium determinations the reaction becomes a source of error due to the precipitation of uranium in an insoluble form. In the solution of the ammonium salt, dissociation occurs, the result being the formation of small amounts of base. This reacts with the uranium to precipitate the bright yellow uranate in an insoluble form.

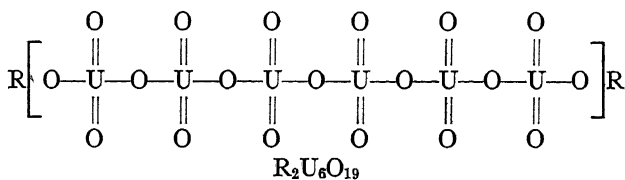
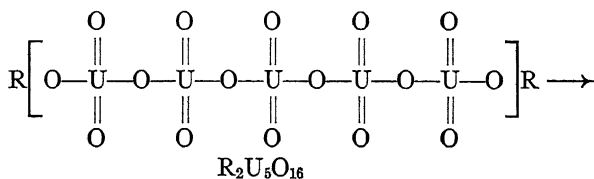
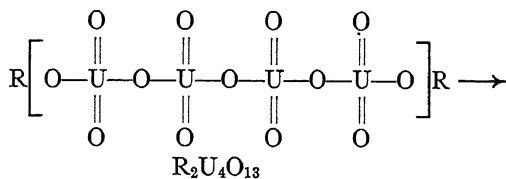
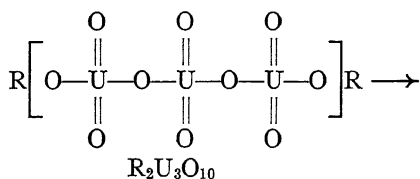
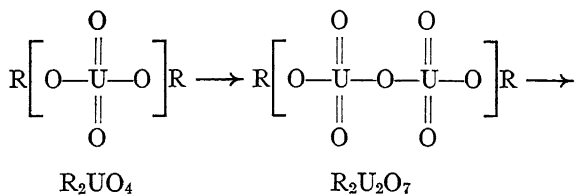
The *uranates* containing hexavalent uranium are regarded as being mainly derived from metauranic acid, H_2UO_4 , the anhydride of which is UO_3 together with the more complex polyuranates:



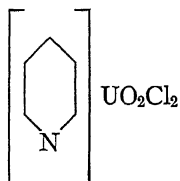
All may be regarded as derivable from the simple uranate, $[R_2UO_4]$ by successive replacement of oxygen by UO_4 or by

alternatively repeated addition of UO_3 , the series being ascended as shown in the accompanying diagram.

Ascension of the Uranates

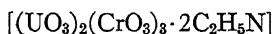


Organo-uranium compounds with the hexavalent element have been prepared, viz.,



and others: $\text{K}_2[\text{UO}_2(\text{C}_2\text{O}_4)_2]$ and $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$.

As contrasted to the above pyridine complex a compound involving uranium in another valence state was prepared in 1907 by Briggs containing pyridine:



Reactivity and Special Properties

Uranium is fairly reactive, resembling iron in many of its chemical properties (Mellor). The metal does not occur free in nature but it is striking to note that uranium is nearly as abundant in nature as copper. It is itself a lustrous white malleable metal possessing a number of well-defined properties (see table).

The isotopes of uranium in metallic form will doubtless have properties closely related if not identical, in most instances, to those ascribed to ordinary uranium—the mixture of isotopes. Therefore, the properties of uranium metal in this section and especially a number of those in the accompanying table, may be assumed to hold in close approximation for uranium whether it is the ordinary entity comprised of the various isotopes, or whether the deportment of isolated uranium 238 or pure uranium 235 is being considered. It is noteworthy that few radical departures from the usual properties attributed to other elements are noted in the pure isotopes of these other elements.

Uranium is capable of taking a high polish and burns

briskly in air at 170°C . to form the lower dioxide, UO_2 . It is stable in dry air but in moist air it slowly oxidizes. Gases such as helium and argon are not freely soluble in the metal but hydrogen dissolves in it to the extent of about 1.6 mg. in every 100 gm. of metal at 1100°C . and 760 mm. pressure.

PROPERTIES OF URANIUM

Color.....	White (massive)
Fracture.....	Bright
Polish.....	White with bluish tinge
Luster.....	Silvery
Ductility.....	High
Melting point.....	1850°C . or thereabouts
Density.....	18.685 at 13°C .
Hardness.....	B-92 to B-94 (Rockwell, fused)
Specific heat.....	0.0276 at 0°C .
Atomic heat.....	6.57 at 0°C .
Atomic volume.....	12.84
Resistivity.....	$.60 \times 10^{-6}$ ohm at 20°C .
Entropy.....	10.5 to 15.37
Magnetic susceptibility.....	$+3.26$ to 4.34×10^{-6} m.u.
Atomic absorption coefficient....	1123 (water = 1)
Oxidizing temperature.....	170°C .
Heat of oxidation $\longrightarrow \text{UO}_3$	303.9 cal.
Vibration frequency.....	3.13×10^6
Atomic radius U^{IV}	0.97 to 1.05 A.U.
Mean mass number.....	237.977

Uranium burns in fluorine and chlorine, the ignition temperature being between 150 and 180°C . The ignition temperature for uranium in an atmosphere of iodine is 260°C . In an atmosphere of bromine it ignites between 210 and 240°C . Uranium halides are the end-products in these reactions. Uranium metal is attacked by hydrogen halides to form halide salts.

The powdered metal is gray to black in color and slowly reacts with cold water and more quickly with hot water.

It is not perceptibly affected by concentrated alkalis, e.g., potassium hydroxide and sodium hydroxide solutions. The purified metallic isotopes will doubtless be identical in these respects.

Uranium metal combines with fused sulfur and selenium. With carbon the carbide is formed. It dissolves in mineral acids, liberating hydrogen during the course of the reaction, also forming a uranous salt. Uranium displaces mercury, silver, copper, tin, platinum, and gold from solutions of their salts.

Uranium has a great affinity for nitrogen, forming on combination, the nitride. This is sometimes an obstacle in the preparation of the pure element. The reaction occurs at 1000°C . (I. Zscherkoff) and nitrogen is re-evolved when the material is exposed to cathode radiation. With ammonia gas the reaction with uranium is accompanied by incandescence. On the other hand, little reaction occurs between uranium and ammonium hydroxide (cf. action of alkalis on the metal).

Moissan first directed attention to the magnetic properties of uranium in 1893. He stated that uranium was not magnetic when free from iron. However, more precise determinations of the magnetic susceptibility of uranium show it to be only very slightly paramagnetic, an exact value being shown in the table.

One of the first determinations of the magnetic susceptibility of uranium ions was made in 1909 by Pascal. In these investigations a molal susceptibility of 3375×10^{-6} for the uranous ion in 10% sulfuric acid was obtained. Later, in 1928, magnetic measurements were made on solid uranous oxalate and uranyl nitrate at 20°C . Similar determinations were made in 1915 by Wedekind and Horst. Sucksmith (1932) determined magnetic susceptibilities of solid uranium

tetrachloride and uranous sulfate from 90° K. to temperatures somewhat above room temperature.

In 1934 Robert W. Lawrence used a modified Gouy method which had been described by Freed in 1927 to determine the magnetic susceptibilities of tetravalent and trivalent uranium ions in solution. In his studies Lawrence used a glass cylinder filled with nickel chloride solution, suspended from a knife edge in a bath which consisted of a solution containing the material to be determined. The end of the tube was at the end of the pole-gap of an electromagnet. The tubes were standardized by balancing them against solutions which had been analyzed to ascertain their nickel chloride concentration. Data was thus obtained for the known susceptibilities of nickel chloride and water, the solution to be determined, and also the magnetic equivalent susceptibility of the tubes used. The calibrated tubes were then used to determine the susceptibilities of uranium solutions (cf. postulation in isotope section on highly susceptible molecules).

Lawrence used Wiedemann's Law for calculating the magnetic susceptibilities of the solutions. In this law the magnetic susceptibility of a solution is an additive function of the susceptibilities of the constituents of the solution. The results obtained during these studies were converted into magnetic moments expressed in Bohr units which were then compared with theoretical magnetic moments.

Experimental magnetic moments in Bohr magnetons found were:

- 2.97 for U^{IV} as the chloride
- 2.95 for the U^{IV} as the sulfate and perchlorate
- 2.73 for UO_2^{++}
- 3.22 for U^{III} as the chloride

The total mass absorption coefficient of uranium for X-rays has been determined. In the accompanying table values are given for various wavelengths of X-radiation.

TOTAL MASS ABSORPTION COEFFICIENT (URANIUM)

After N. Lange, Based on Density (ρ) = 18.7

$\lambda = A.U.$	μ/ρ
0.095.....	3.53
0.113.....	1.78
0.126.....	1.90
0.14.....	2.56
0.151.....	3.78
0.164.....	3.24

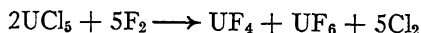
A fact of importance was revealed in the investigations of A. S. Russel in 1931. In addition to being directly pertinent to analytical procedures for uranium this may be of significance with the recent developments in nuclear fission or other aspects of nuclear physics. The studies involved deposition of reactive metals on noble metals. Uranium was deposited on a mercury surface, according to the Nernst Theory of Electrode Potential, when acidified solutions of its salts were shaken with mercury amalgam.

The presence of very slight concentrations of the metal is detected by the catalytic effect on the evolution of hydrogen from sulfuric acid by pure zinc. The surface deposited uranium is insoluble in the mercury. The same investigator determined the solubility of uranium in mercury as greater than one in 10^7 (studies with N. M. Irvin in 1932). G. Tamman and J. Hinnuber determined the solubility of uranium in mercury as 0.00014% at 20° C. The deposition of metals other than uranium occurs also. Titanium, tungsten, and molybdenum may be studied by these means as well as uranium. It would appear from this that Group Six elements, i.e., the chromium series, may be correlated as a whole

with this action. This principle holds possibilities as the basis for a system of analysis.

Uranium Halides

The halogen derivatives of uranium have been discussed briefly in the section on valency and series ascension. Important non-oxygenated fluorides are as follows: uranium difluoride ($\text{UF}_2 \cdot 2\text{H}_2\text{O}$); uranium tetrafluoride (UF_4); and, uranium hexafluoride (UF_6). The tetrafluoride is stable only at low temperatures, being prepared from UCl_5 as follows:

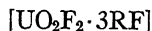


The hexafluoride is removed by distillation and at 20°C . the tetrafluoride oxidizes to the uranyl salt, UO_2F_2 . A monohydrate of uranium tetrafluoride, $\text{UF}_4 \cdot \text{H}_2\text{O}$ is known. The double fluoride, an important commercial uranium salt, KUF_5 is obtained by the reduction of alkali uranyl fluoride solutions with formic acid in light (Bolton, 1886).

Two oxygenated fluorine derivatives of uranium involve the U^{4+} and uranyl radicals, e.g., UOF_2 , this being produced by the reaction between hydrofluoric acid and U_3O_8 . The other compound, UO_2F_2 is obtained by:



These compounds lead up to the complex double uranyl fluorides:



where $\text{R} = \text{K}$ or NH_4 in now described compounds.

Uranium chloride, UCl_3 , is soluble in water, forming a red-brown solution which is unstable. The compound is obtained by reduction of uranyl salts in hydrochloric acid solution with nascent hydrogen. Two other non-oxygenated

uranium chlorides are: UCl_4 and UCl_5 . The tetrachloride is obtained by heating a uranium compound in chlorine (see data elsewhere in this chapter). The substance leads to complex double chlorides:



where $\text{R} = \text{Na}, \text{K}, \text{Li}$, or $\text{R}_2 = \text{Ca}, \text{Sr}$, or Ba . The double chlorides are prepared by passing UCl_4 vapor over chlorides of R at red heat. The double chlorides are relatively unstable.

Oxygenated chlorine compounds of uranium include uranyl chloride, UO_2Cl_2 and two chlorates: uranyl chlorate, $\text{UO}_2(\text{ClO}_3)_2 \cdot x\text{H}_2\text{O}$ and uranyl perchlorate, $\text{UO}_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ where n may be 6 or 4. Uranyl chloride may be prepared by the action of chlorine on hot uranous oxide, the product obtained being stable, very hygroscopic and soluble in water. Mono and trihydrate forms are known in addition to the anhydride. Uranyl chloride forms double salts:



where R may be $\text{Rb}, \text{K}, \text{NH}_4$, or Cs .

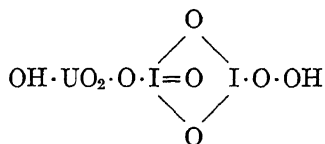
Uranium bromide, UBr_4 , in the form of a vapor was used by Nier in his mass-spectroscopic studies on the isotopes of uranium. The compound may be prepared by passing bromine vapor over hot uranium metal in an inert atmosphere. Uranium bromide forms double salts:



These may be obtained by passing vaporized uranium bromide over hot alkali bromides.

An unstable compound, uranyl bromate is known and the bromide, UO_2Br_2 may be obtained when bromine vapor is passed over uranous oxide at an elevated temperature, the other bromide also being formed in the reaction.

Uranium iodide is obtained from uranium and iodine when heated together at $500^{\circ}\text{C.} \rightarrow \text{UI}_4$. Unstable crystals characterize uranyl iodide, UO_2I_2 . Uranyl iodate is of more interest since it occurs in two modifications; the rhombic-prismatic and the pyramidal. The former modification is converted into the latter on heating at 100°C. When crystallized from hot solutions the monohydrate, $\text{UO}_2(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ is obtained while from hot solutions crystals of $\text{UO}_2(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$ are obtained. The structure of the monohydrate has been stated by Artman to be:



Uranium Oxides

From many standpoints the oxides of uranium are very important. Uranium often occurs in nature in the form of one or more of its oxides. Of these oxides there are two chief types, the basic oxide UO_2 and an acid anhydride UO_3 . An intermediate oxide, known as U_3O_8 is of much interest and importance. Two other oxides have been described but it is not known with certainty whether they exist or not since one, UO , is based on bivalent uranium which has been practically disproven by recent studies. The other, UO_4 , probably exists since it has well known derivatives, i.e., the peruranates.

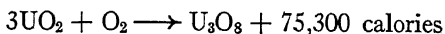
The higher oxides are described further in this chapter. Uranoous oxide (UO_2) may be obtained by a number of methods. R. H. Vallance and A. A. Eldridge (1926) enumerated eighteen:

- (1) By the reduction of U_3O_8 (Arfvedson, 1823).
- (2) By the reduction of uranyl oxalate with hydrogen (Peligot, 1842).

- (3) By ignition of one or more of the higher oxides in an inert atmosphere, e.g., nitrogen or carbon dioxide (Zimmermann, 1886).
- (4) By heating U_3O_8 with ammonium chloride (Smith and Matthews, 1895).
- (5) By heating U_3O_8 with ammonium chloride and sulfur (Hermann, 1861).
- (6) By heating U_3O_8 with anhydrous oxalic acid.
- (7) By reduction of uranyl sulfate or nitrate with hydrogen (Lebeau, 1912).
- (8) By heating a mixture of uranyl phosphate with potassium carbonate and potassium cyanide (Rose, 1862).
- (9) By the electrolysis of a solution of uranyl nitrate (O. de Coninck and Camo, 1901).
- (10) By reduction of a solution of uranyl chloride with powdered aluminum or powdered magnesium (O. de Coninck, 1909).
- (11) By reduction of U_3O_8 with carbon or by heating slightly with hydrofluoric acid (Ditte, 1880).
- (12) By heating crystallized uranic hydroxide in hydrogen (Aloy, 1900).
- (13) By heating uranyl chloride with potassium in hydrogen (Arfvedson).
- (14) By heating uranyl chloride with a mixture of ammonium chloride and sodium chloride (Wahler, 1842).
- (15) By heating Na_2UCl_6 in a humid atmosphere of carbon dioxide (Colani, 1903).
- (16) By fusion of sodium diuranate with four parts of magnesium chloride (Hofmann and Hörschle, 1915).
- (17) By calcining uranyl bromide, UO_2Br_2 , in air (O. de Coninck, 1902).

- (18) By fusion at red heat a mixture of sodium chloride, sodium uranate and charcoal.

Uranous oxide reacts with chlorine and bromine to form the corresponding uranyl halide. Uranous oxide melts at 2176°C . (Ruff and Goeche, 1911) in an atmosphere of nitrogen and is soluble with difficulty in dilute hydrochloric and sulfuric acids although it slowly dissolves in nitric acid and aqua regia. At 185°C . reaction begins which results in the higher oxide U_3O_8 . The oxidation of uranous oxide is:



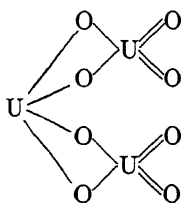
The hydrated uranous oxide is known as uranous hydroxide of which two varieties are known, the monohydrate and the dihydrate. Uranous hydroxide may be prepared by the addition of an alkali to tetravalent uranium ions in solution, this reaction forming a precipitate which, after drying, consists of the black $\text{UO}_2 \cdot \text{H}_2\text{O}$. Uranous hydroxide is unstable and is readily oxidized to uranyl salts.

Although the existence of uranium pentoxide, U_2O_5 has been seriously questioned its existence has probably been confirmed by the studies of Schwarz in 1920. The pentoxide was first noted in 1842 by Peligot who described it as a black product obtained when the uranium salt of a volatile acid was strongly ignited in air. It is interesting to note, however, that Zimmermann, Colani, and others in the field of uranium chemistry regarded this compound as a mixture of uranous oxide and U_3O_8 . The material was prepared in two different ways by de Coninck in 1901–1903. The first procedure used by this investigator consisted of electrolyzing a solution of uranyl nitrate. The other technique consisted of heating hydrated ($3\text{H}_2\text{O}$) uranyl sulfate. Janda (1901) regarded it possible to prepare U_2O_5 by heating ammonium peruranate, $[(\text{NH}_4)_2\text{U}_2\text{O}_7] \cdot 6\text{H}_2\text{O}$, in a carbon crucible.

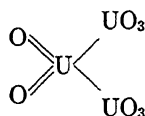
The most important oxide of uranium is the green oxide, *urano-uranic oxide*, U_3O_8 , which occurs to a large extent in pitchblende. The material is an amorphous green substance although it may also be black. In connection with green and black colored U_3O_8 it is noted that both appear green on a streak plate (Remele, 1865). Urano-uranic oxide is insoluble in water and dilute acids but in concentrated acids it slowly dissolves to U^{IV} and UO_2 salts. Since it is quite stable to high temperatures it may therefore be conveniently used in gravimetric analysis or in procedures involving fire assay or high temperatures.

While the composition of *uraninite* has been interpreted on the basis of UO_2 by a number of studies, the composition of *pitchblende* is U_3O_8 , the exact structure for the latter not being known with certainty. In the accompanying diagrams structural formulae for four different forms of U_3O_8 are shown. The first two (I and II) are the preferred forms while III is a structure based on bivalent uranium (Groth) and IV may be regarded as being based on U_2O_5 , i.e., $\text{UO}_2(\text{U}_2\text{O}_5)$ or as having two uranyl radicals, i.e., $\text{UO}_3 \cdot \text{O}(\text{UO}_2)_2$, with an oxygen bridge attached with a bond to each uranyl group. The existence of the last two structures is extremely questionable.

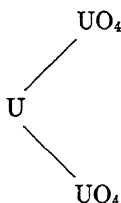
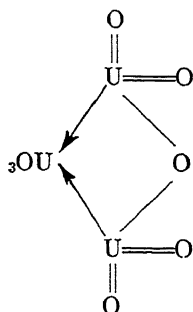
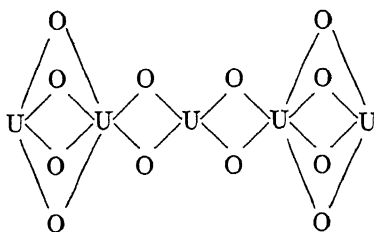
C. W. Blomstrand regarded uraninite as a derivative of hexabasic orthouranic acid, $[\text{U}(\text{OH})_6]$, in which the hydrogen is replaced by tetravalent uranium:



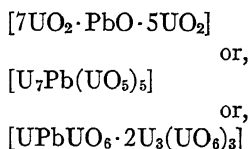
(I) U_3O_8 as $\text{UO}_4(\text{UO}_2)_2$



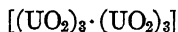
(II) U_3O_8 as $\text{UO}_2(\text{UO}_3)_2$

(III) U_3O_8 as $\text{U}(\text{UO}_4)_2$ (IV) U_3O_8 as $\text{UO}_3(\text{U}_2\text{O}_5)$ 

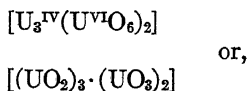
to true pitchblende being ascribed a formula which contains lead:



The composition of uraninite from Katanga was given the following formula by A. Schoep:

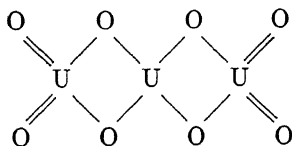


Blomstrand's formula for uraninite:



was found by Hillebrand to be not too general in application.

The construction of urano-uranic oxide has been ascribed by Zinnier:



Pure green oxide of uranium is valuable for numerous purposes. In research it provides a starting point for many investigations which involve uranium and in nuclear physics its value as "raw material" for light isotopes is apparent. A number of methods have been described for the preparation of this substance. Among them are:

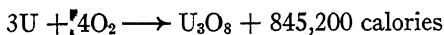
(1) By heating at red heat any oxide (McCoy and Ashman, 1908).

(2) By the ignition of ammonium diuranate at 900° C. (Colani, 1907).

(3) By heating to red heat any uranyl salt of a volatile acid.

(4) For the preparation of the pure green oxide of uranium the following method of Giolitti and Tavanti (1904) may be useful: One hundred grams of sodium uranyl acetate are dissolved in a mixture consisting of four liters of water and fifty cubic centimeters of hydrochloric acid. The uranyl salt in solution is then precipitated with three hundred cubic centimeters of concentrated ammonium hydroxide. The precipitate is washed ten or more times with two per cent ammonium chloride solution and then redissolved in hydrochloric acid, the procedure being repeated twice. Finally the wet precipitate is calcined and recovered as U₃O₈.

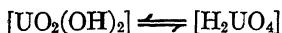
The heat of formation of U₃O₈ was determined in 1912 by Mixer:



When a uranyl salt is mixed with practically any readily oxidizable substance of an organic nature and exposed to light a violet precipitate of U_3O_8 is formed. This was first observed by Ebelman in 1842. The material thus prepared, however, has acid in it but on boiling with water the hydrated U_3O_8 of Aloy and Rodin (1920) is obtained, $U_3O_8 \cdot H_2O$. The violet precipitate has been of much interest and many investigations based on it have been performed, e.g., studies in photolysis.

Uranic oxide, UO_3 is another of the oxides of uranium also being known as uranic anhydride, uranyl oxide, and uranium trioxide. It exists in two modifications, the orange-yellow and the red, the latter of which may be regarded as a polymeride of the former (O. de Coninck, 1901). Both substances are amorphous and on heating the orange-yellow form the red form is obtained.

Uranic oxide may be obtained by heating ammonium uranyl carbonate or uranic acid to $300^\circ C$. When uranic oxide itself is heated in air $1\frac{1}{2}$ molecules of oxygen are evolved and U_3O_8 is obtained (Brunck). In hydrogen, at elevated temperatures, it is reduced to the lower oxide UO_2 . With carbon at $3000^\circ C$. the oxide is completely reduced to uranium metal (Moissan, 1892). It is slightly basic with the exception of UF_6 and its salts contain $\frac{2}{3}$ of the oxygen present in the original oxide (UO_3) in the form of UO_2 , i.e., UO_2R_2 . It acts towards bases as an acid anhydride producing, on reaction, stable uranates and with water producing uranyl hydroxide, $UO_2(OH)_2$, the latter compound being also known as uranic acid, an amphoteric substance:



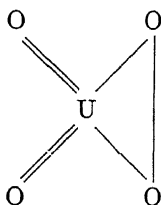
Vallance and Eldrige have enumerated methods of preparation for uranic acid:

- (1) By heating an alcoholic solution of uranyl nitrate and washing the precipitate with hot water.

- (2) By exposure of uranyl oxalate to light until the precipitate becomes yellow.
- (3) By heating $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ in dry air at 80°C .
- (4) By exposure of the violet hydrate to air and then boiling in water for several hours.
- (5) By heating a two per cent solution of uranyl acetate in a sealed tube for one hundred hours at 175°C .
- (6) By digestion of a mixture of copper hydroxide and a solution of uranyl nitrate.

Two hydrates of uranic anhydride are known: $\text{UO}_3 \cdot \text{H}_2\text{O}$ and $\text{UO}_3 \cdot 2\text{H}_2\text{O}$.

It is doubtful whether uranium tetraoxide, UO_4 , exists in the anhydrous form. However, a hydrate of UO_4 is known, $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. Also, an acid derivative exists, peruranic acid, which combines to form well-defined salts. The salts, peruranates, may be obtained by the reaction of hydrogen peroxide with uranyl ions in alkaline solutions. Peruranates are soluble in water but are precipitated by alcohol and other organic liquids. Their structures are not known exactly, various formulae being ascribed to the UO_4 which serves as their basis:



(Melikoff and Pissarjewsky)

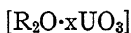
as well as $[(\text{UO}_3)_2\text{UO}_6]$, (Fairly, 1877).

The *peruranates* have the general formulae:

- (1) $[(\text{RO}_2)_2 \cdot \text{UO}_4] \cdot n\text{H}_2\text{O}$
- and,
- (2) $[(\text{RO}_2)_2(\text{UO}_4)_2] \cdot n\text{H}_2\text{O}$

Where R may be two monovalent cations such as NH_4 , Li, K, or Na, or perhaps a combination. R may also be a bivalent cation such as Ba, Ca, Cu, Pb, or Ni. The value of n varies from 1 to 10 for compounds now known.

Uranic acid is a dibasic acid important because it forms salts of the R_2UO_4 type as well as higher salts which are richer in acid content (for data on the ascension of the series to form polyuranates see data under the valence discussion). On the basis of UO_3 the salts of the alkali metals are of the following type:



where x is known to be from 1 to 6 in compounds so far studied.

Monouranates, $[\text{R}_2\text{O} \cdot \text{UO}_3]$, are known with R as: (NH_3OH) ; Ba; Bi; Ca; Fe; Li; Mg; Nd; K; Rb; Na; Sr; and, Zn. *Diuranates* are more important uranium compounds. They may be obtained by the addition of carbonates, hydroxides, or metallic oxides to solutions containing uranyl ions as contrasted to the monuranates which may be obtained by fusion. Diuranates are insoluble yellow materials which dissolve in acids. Their structure, $[\text{R}_2\text{O} \cdot 2\text{UO}_3]$, may contain the following elements as R: NH_4 ; Ba; Ca; K; Ag; and, Na.

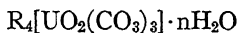
Triuranates, $[\text{R}_2\text{O} \cdot 3\text{UO}_3]$, are known with $\text{R} = \text{Na}$; *tetrauranates*, $[\text{R}_2\text{O} \cdot 4\text{UO}_3]$, are known with $\text{R} = \text{K}$; *pentauranates*, $[\text{R}_2\text{O} \cdot 5\text{UO}_3]$, are known with $\text{R} = \text{K}$ and Na; and, *hexauranates*, $[\text{R}_2\text{O} \cdot 6\text{UO}_3]$, may have the following elements as R: NH_4 ; K; and, Na.

Uranium Carbonates

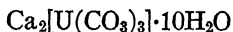
Uranium occurs in nature rather extensively in the form of complex carbonates, this being evidenced by the many radioactive minerals which contain both the uranyl group and the

carbonate group in their make-up. Uraniferous carbonates are always of secondary origin and are formed by alteration of pitchblende and/or uraninite.

The lowest compound of uranium containing carbon is the carbide, first prepared by Moissan in 1896 by electric furnace methods. The carbide of uranium has been mentioned previously. *Rutherfordine*, a naturally occurring uranium and carbon compound, is uranyl carbonate, UO_2CO_3 and has apparently not yet been prepared artificially. Attempts to prepare artificial rutherfordine have failed since the reaction between alkaline carbonate solutions and uranyl salts form several substances which are variable, basic uranates and carbonates being among the main end-products. However, uranyl carbonate serves to introduce two series of more complex uranyl carbonates, i.e., double salts, one series of which may be represented by:



The two important members of this series are *liebigite*, $\text{R} = \text{Ca}$ and $n = 20$; and, *voglite*, $\text{R} = \text{Cu}$ and n varies. In addition to these a number of salts have been prepared in the laboratory which have not been found to occur naturally: $\text{R} = \text{NH}_4 (n = 2)$; $\text{K} (n = 0)$; $\text{Na} (n = 0)$; and, $\text{Tl} (n = 0)$. A related uranium and carbonate complex is *uranothallite* which does not follow the above general formula closely but has the structure:



The second series of complex uranyl carbonates may be represented by:



of which only one compound appears to have been described: $\text{R} = \text{NH}_4$ with $n = 4$.

URANIUM CARBONATES

<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Uranous carbonate.....	_____	H. Rose (1)
Ammonium uranous carbonate.....	_____	J. Arvedson (2)
Uranyl carbonate.....	$[(\text{UO}_2)\text{CO}_3]$	E. Peligot (3)
Uranyl decahydroxy- tricarboxylate.....	$[8\text{UO}_2(\text{OH})_2 \cdot \text{CO}_3] \cdot 6\text{H}_2\text{O}$	K. Seubert (4)
RUTHERFORDITE.....	$[(\text{UO}_2)\text{CO}_3]$	W. Marckwald (5)
Ammonium uranyl tricarboxylate.....	$(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3] \cdot 2\text{H}_2\text{O}$	J. Berzelius (6)
Ammonium diuranyl pentacarboxylate.....	$[2(\text{UO}_2)\text{CO}_3 \cdot 3(\text{NH}_4)_2\text{CO}_3]$	F. Giolitti (7)
Ammonium octauranyl heptadecacarboxylate...	$(\text{NH}_4)_{18}[(\text{UO}_2)_8(\text{CO}_3)_{17}]$	F. Giolitti (7)
Sodium uranyl tricarboxylate.....	$\text{Na}_4[(\text{UO}_2)(\text{CO}_3)_3]$	J. Ebelmen (8)
Potassium uranyl tricarboxylate.....	$\text{K}_4[(\text{UO}_2)(\text{CO}_3)_3]$	J. Ebelmen (8)
Silver uranyl tricarboxylate.....	$\text{Ag}_4[(\text{UO}_2)(\text{CO}_3)_3]$	J. Hedvall (9)
Calcium uranyl tetracarboxylate.....	$\text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_4]$	J. Vogl (10)
URANTHALITE.....	$\text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_4] \cdot 10\text{H}_2\text{O}$	A. Schrauf (11)
Calcium uranyl dicarbonate icosihydrate.....	$\text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_4] \cdot 20\text{H}_2\text{O}$	J. Vogl (12)
LIEBIGITE.....	$[\text{CaO} \cdot \text{UO}_3 \cdot 2\text{CO}_2] \cdot 20\text{H}_2\text{O}$	J. Smith (13)
Calcium uranyl dicar- bonate decahydrate..	$\text{Ca}[(\text{UO}_2)(\text{CO}_3)_2] \cdot 10\text{H}_2\text{O}$	C. Blinkoff (14)
Calcium tetrauranyl tricarboxylate.....	$[2\text{CaO} \cdot 4\text{UO}_3 \cdot 3\text{CO}_2] \cdot 22\text{H}_2\text{O}$	A. Schrauf (15)
SCHROECKINGERITE...	$[2\text{CaO} \cdot 4\text{UO}_3 \cdot 3\text{CO}_2] \cdot 22\text{H}_2\text{O}$	A. Schrauf (15)
DAKEITE.....	$[3\text{CaO} \cdot \text{UO}_2(\text{SO}_3) \cdot 3\text{CO}_2] \cdot 10\text{H}_2\text{O}$	E. Larsen (16)
		Cf. Schrauf (15)
RANDITE.....	_____	G. Konig (17)
Copper calcium uranyl carbonate.....	_____	J. Vogl (18)
VOGLITE.....	_____	W. Haidinger (19)
Strontium diuranyl dicarbonate.....	$[\text{SrO} \cdot 2\text{UO}_3 \cdot 2\text{CO}_2] \cdot 10\text{H}_2\text{O}$	C. Blinkoff (20)
Barium uranyl carbonate.....	$\text{Ba}_2[(\text{UO}_2)(\text{CO}_3)_3] \cdot 6\text{H}_2\text{O}$	J. Hedvall (21)

URANIUM CARBONATES (*Continued*)

<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Barium diuranyl dicarbonate pentahydrate.	$[\text{BaO} \cdot 2\text{UO}_3 \cdot 2\text{CO}_2] \cdot 5\text{H}_2\text{O}$ C. Blinkoff (22)
Barium diuranyl dicarbonate octahydrate.	$[\text{BaO} \cdot 2\text{UO}_3 \cdot 2\text{CO}_2] \cdot 8\text{H}_2\text{O}$ C. Blinkoff (22)
Thallos uranyl tricarbate.	$\text{TL}_4[(\text{UO}_2)(\text{CO}_3)_3]$ H. Behrens (23)
Ammonium uranium tetracarbate.	$(\text{NH}_4)_2[\text{U}(\text{CO}_3)_4] \cdot 6\text{H}_2\text{O}$ B. Menes (24)
Guanidinium uranium tetracarbate.	$(\text{CN}_3\text{H}_6)_2[\text{U}(\text{CO}_3)_4] \cdot 10\text{H}_2\text{O}$ B. Menes (24)

Note: the literature cited will be found at the end of this chapter.

Uranium Phosphates

Compounds of uranium and phosphorus are interesting from an analytical standpoint. The presence of phosphoric acid greatly interferes with analysis for uranium in minerals. There are many radioactive minerals which contain phosphorus and most of them contain the uranium in the hexavalent state as the uranyl group and all contain phosphorus as the phosphate.

As would be expected, the greater part of these minerals are complex double salts although a few, *uranospathite*, for example, can be regarded as relatively simple materials, i.e., uranyl phosphate. Generally, the uranium phosphates are highly fluorescent and all of them are secondary uranium minerals. Species like *autunite* contain calcium as the other important element besides uranium, phosphorus and oxygen. In antithesis, minerals like *renardite*, *parsonite*, and *chalcophile*, contain heavy metals like lead, copper, or others.

The simplest uranium-phosphorus compound is uranium metaphosphide, UP, which is obtained in the complex mixture of uranium and phosphorus compounds which result when uranyl hypophosphite is heated. Another compound, uranous phosphide, U_3P_4 , oxidizes to uranyl phosphate.

URANIUM PHOSPHATES

<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Uranous orthophosphate.....	$[\text{U}_3(\text{PO}_4)_4]$	A. Colani (1)
Uranous orthophosphate trihydrate.....	$[\text{U}_3(\text{PO}_4)_4] \cdot 3\text{H}_2\text{O}$	P. Chaistaing (2)
Uranous oxyphosphate.....	$[\text{U}_2\text{O}(\text{PO}_4)_2]$	A. Colani (1)
Uranous oxyphosphate trihydrate.....	$[\text{U}_2\text{O}(\text{PO}_4)_2] \cdot 3\text{H}_2\text{O}$	P. Chaistaing (2)
Uranous oxyphosphate tetrahydrate.....	$[\text{U}_2\text{O}(\text{PO}_4)_2] \cdot 4\text{H}_2\text{O}$	P. Chaistaing (2)
Uranous hydrophosphate.....	$[\text{U}(\text{HPO}_4)] \cdot 2\text{H}_2\text{O}$	J. Alloy (3)
Uranous hydrophosphate pentahydrate.....	$[\text{U}(\text{HPO}_4)] \cdot 5\text{H}_2\text{O}$	J. Alloy (3)
Uranous pyrophosphate.....	$[\text{U}(\text{P}_2\text{O}_7)]$	C. Rammelsberg (4)
Uranous pyrophosphate trihydrate.....	$[\text{U}(\text{P}_2\text{O}_7)] \cdot 3\text{H}_2\text{O}$	C. Rammelsberg (4)
Uranous metaphosphate.....	$[\text{U}(\text{PO}_4)_4]$	Hautefeuille (5)
Sodium uranous diphosphate.....	$\text{Na}_2[\text{U}_2(\text{PO}_4)_2]$	A. Colani (1)
Sodium uranous triphosphate.....	$\text{Na}_2[\text{U}_2(\text{PO}_4)_3]$	A. Colani (1)
Sodium uranous octaphosphate.....	$\text{Na}_{12}[\text{U}_3(\text{PO}_4)_8]$	A. Colani (1)
Potassium uranous diphosphate.....	$\text{K}_2[\text{U}(\text{PO}_4)_2]$	A. Colani (1)
Potassium uranous triphosphate.....	$\text{K}[\text{U}_2(\text{PO}_4)_3]$	A. Colani (1)
Potassium uranous octaphosphate.....	$\text{K}_{12}[\text{U}_3(\text{PO}_4)_8]$	A. Colani (1)
Calcium uranous diphosphate.....	$\text{Ca}[\text{U}(\text{PO}_4)_2]$	A. Colani (1)
Strontium uranous diphosphate.....	$\text{Sr}[\text{U}(\text{PO}_4)_2]$	A. Colani (1)
Barium uranous diphosphate.....	$\text{Ba}[\text{U}(\text{PO}_4)_2]$	A. Colani (1)
Uranyl orthophosphate.....	$[(\text{UO}_2)_3(\text{PO}_4)_2]$	G. Werther (6)
PHOSPHOURANYLITE.....	$[(\text{UO}_2)_3(\text{PO}_4)_2] \cdot 6\text{H}_2\text{O}$	F. Genth (7)
Uranyl hydrophosphate trihydrate.....	$[\text{UO}_2(\text{HPO}_4)] \cdot 3\text{H}_2\text{O}$	G. Werther (6)
Uranyl hydrophosphate hemitrihydrate.....	$[2(\text{UO}_2)\text{HPO}_4] \cdot 4\text{H}_2\text{O}$	G. Werther (6)
Uranyl hydrophosphate tetrahydrate.....	$[(\text{UO}_2)\text{HPO}_4] \cdot 4\text{H}_2\text{O}$	L. Bourgeois (8)

URANIUM PHOSPHATES (*Continued*)

<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Uranyl hydrophosphate hemienneahydrate.....	$[\text{UO}_2(\text{HPO}_4)] \cdot 4\frac{1}{2}\text{H}_2\text{O}$	A. Langier (9)
Uranyl hydrophosphate heptahydrate.....	$[\text{UO}_2(\text{HPO}_4)] \cdot 7\text{H}_2\text{O}$	H. Lienau (10)
Uranyl dihydrophosphate.....	$[\text{UO}_2(\text{H}_2\text{PO}_4)] \cdot 3\text{H}_2\text{O}$	G. Werther (6)
Uranyl pyrophosphate.....	$[(\text{UO}_2)_2(\text{P}_2\text{O}_7)]$	R. Arendt (11)
Uranyl pyrophosphate enneahydrate.....	$[(\text{UO}_2)_2\text{HPO}_4] \cdot 4\text{H}_2\text{O}$	R. Arendt (11)
Uranyl pyrophosphate decahydrate.....	$[\text{UO}_2(\text{HPO}_4)] \cdot 4\frac{1}{2}\text{H}_2\text{O}$	R. Arendt (11)
Uranyl pyrophosphate pentadecahydrate.....	$[\text{UO}_2(\text{HPO}_4)] \cdot 7\text{H}_2\text{O}$	R. Arendt (11)
Uranyl pyrophosphate tetrahydrate.....	$[(\text{UO}_2)_2(\text{P}_2\text{O}_7)] \cdot 4\text{H}_2\text{O}$	P. Chaistaing (2)
Uranyl pyrophosphate monohydrate.....	$[(\text{UO}_2)_2\text{P}_2\text{O}_7] \cdot \text{H}_2\text{O}$	P. Chaistaing (2)
Uranyl oxymetaphosphate.....	$[4\text{UO}_3 \cdot 3\text{P}_2\text{O}_5]$	P. Chaistaing (2)
Uranyl metaphosphate.....	$[\text{UO}_2(\text{PO}_3)_2]$	C. Rammelsberg (4)
Uranyl tetrphosphate.....	$[\text{UO}_3 \cdot 2\text{P}_2\text{O}_5]$	P. Chaistaing (2)
Ammonium uranyl phosphate.....	$\text{NH}_4[(\text{UO}_2)\text{PO}_4] \cdot 3\text{H}_2\text{O}$	R. Arendt (11)
Methylamine uranyl phosphate.....	$[(\text{CH}_3)\text{NH}_2(\text{UO}_2)\text{PO}_4]$	L. Barthe (12)
Ethylamine uranyl phosphate.....	$[(\text{C}_2\text{H}_5)\text{NH}_2(\text{UO}_2)\text{PO}_4]$	L. Barthe (12)
Trimethylamine uranyl phosphate.....	$[(\text{CH}_3)_3\text{NH}(\text{UO}_2)\text{PO}_4]$	L. Barthe (12)
Lithium uranyl phosphate... ..	$\text{Li}[(\text{UO}_2)\text{PO}_4]$	H. Lienau (13)
Sodium uranyl phosphate... ..	$\text{Na}[(\text{UO}_2)\text{PO}_4]$	H. Lienau (13)
Potassium uranyl phosphate.....	$\text{K}[(\text{UO}_2)\text{PO}_4]$	L. Ouvard (14)
Potassium uranyl phosphate trihydrate... ..	$\text{K}[(\text{UO}_2)\text{PO}_4] \cdot 3\text{H}_2\text{O}$	H. Lienau (13)
Lithium uranyl pyrophosphate.....	$\text{Li}_2[\text{UO}_2(\text{P}_2\text{O}_7)]$	A. Rosenheim (15)
Lithium uranium pyrophosphate.....	$\text{Li}_2[\text{H}_2\text{U}_2(\text{P}_2\text{O}_7)_3] \cdot 30\text{H}_2\text{O}$	B. Menes (16)
Sodium uranyl pyrophosphate.....	$\text{Na}_2[\text{UO}_2(\text{P}_2\text{O}_7)]$	L. Ouvard (14)
Complex.....	$\text{Na}_6[(\text{UO}_2)_2(\text{P}_2\text{O}_7)_3]$	P. Pascal (17)
Complex.....	$\text{Na}_8[(\text{UO}_2)_2(\text{P}_2\text{O}_7)_3] \cdot 6\text{H}_2\text{O}$	P. Pascal (17)

URANIUM PHOSPHATES (*Continued*)

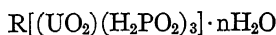
<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Sodium uranium pyrophosphate.	$\text{Na}_4[\text{U}_2(\text{P}_2\text{O}_7)_3] \cdot 14\text{H}_2\text{O}$	B. Menes (16)
Potassium uranyl pyrophosphate.	$\text{K}_2[(\text{UO}_2)_2\text{P}_2\text{O}_7]$	L. Ouvard (14)
Copper uranyl phosphate.	$\text{Cu}[(\text{UO}_2)_2(\text{PO}_4)_2] \cdot 8\text{H}_2\text{O}$	_____
TORBERNITE.	$\text{Cu}[(\text{UO}_2)_2(\text{PO}_4)_2] \cdot 12\text{H}_2\text{O}$	Y. Bucholtz (18)
Cobalt uranyl phosphate.	$\text{Co}[(\text{UO}_2)_2(\text{PO}_4)_2] \cdot 8\text{H}_2\text{O}$	A. Bergman (19)
Calcium uranyl phosphate.	$\text{Ca}[(\text{UO}_2)_2(\text{PO}_4)_2] \cdot 8\text{H}_2\text{O}$	E. Peligot (20)
AUTUNITE.	$\text{Ca}[(\text{UO}_2)_2(\text{PO}_4)_2] \cdot 8\text{H}_2\text{O}$	_____
Calcium autunite.	$[\text{CaO} \cdot 2\text{UO}_3(\text{P}_2\text{O}_5)] \cdot n\text{H}_2\text{O}$	J. Fairchild (21)
Sodium autunite.	_____	J. Fairchild (21)
Potassium autunite.	_____	J. Fairchild (21)
Barium autunite.	$[\text{BaO} \cdot 2\text{UO}_3(\text{P}_2\text{O}_5)] \cdot n\text{H}_2\text{O}$	J. Fairchild (21)
Manganese autunite.	_____	J. Fairchild (21)
Nickel autunite.	_____	J. Fairchild (21)
Copper autunite.	$[\text{CuO} \cdot 2\text{UO}_3(\text{P}_2\text{O}_5)] \cdot n\text{H}_2\text{O}$	J. Fairchild (21)
Magnesium autunite.	$[\text{MgO} \cdot 2\text{UO}_3(\text{P}_2\text{O}_5)] \cdot n\text{H}_2\text{O}$	J. Fairchild (21)
Lead autunite.	$[\text{PbO} \cdot 2\text{UO}_3(\text{P}_2\text{O}_5)] \cdot n\text{H}_2\text{O}$	J. Fairchild (21)
BASSETITE.	_____	A. Hallimond (22)
URANOSPATHITE.	_____	A. Hallimond (22)
Calcium uranyl hydrophosphate.	$[\text{Ca}(\text{UO}_2)(\text{HPO}_4)] \cdot n\text{H}_2\text{O}$	C. Blinkoff (23)
Calcium uranyl hydrophosphate tetrahydrate.	$[\text{Ca}(\text{UO}_2)(\text{HPO}_4)] \cdot 4\text{H}_2\text{O}$	C. Blinkoff (23)
Calcium uranyl hydrophosphate trihydrate.	$[\text{Ca}(\text{UO}_2)(\text{HPO}_4)] \cdot 3\text{H}_2\text{O}$	C. Blinkoff (23)
Calcium uranyl hydrophosphate dihydrate.	$[\text{Ca}(\text{UO}_2)(\text{HPO}_4)] \cdot 2\text{H}_2\text{O}$	C. Blinkoff (23)
Calcium uranyl dioxytetra- phosphate.	$[3\text{CaO} \cdot 5\text{UO}_3 \cdot 2\text{P}_2\text{O}_5] \cdot 16\text{H}_2\text{O}$	C. Blinkoff (23)
Strontium uranyl oxytetraphosphate.	$\text{Sr}_2[(\text{UO}_2)_5\text{O}(\text{PO}_4)_4] \cdot 24\text{H}_2\text{O}$	C. Blinkoff (23)
Strontium uranyl dihydro- tetraphosphate.	$[\text{SrO} \cdot 4\text{UO}_3 \cdot 2\text{P}_2\text{O}_5] \cdot 21\text{H}_2\text{O}$	C. Blinkoff (23)

URANIUM PHOSPHATES (*Continued*)

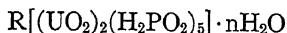
<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Barium uranyl phosphate octahydrate	$\text{Ba}[(\text{UO}_2)_2(\text{PO}_4)_2] \cdot 8\text{H}_2\text{O}$	C. Blinkoff (23)
URANOCIRCITE	$\text{Ba}[(\text{UO}_2)_2(\text{PO}_4)_2] \cdot 8\text{H}_2\text{O}$	A. Weisbach (24)
META-URANOCIRCITE	—	P. Graubert (25)
Lead diuranyl phosphate	$\text{Pb}[(\text{UO}_2)_2(\text{PO}_4)_2]$	A. Schoep (26)
DEWINDITE	$\text{Pb}[(\text{UO}_2)_2(\text{PO}_4)_2]$	A. Schoep (26)
STASITE	$[4\text{PbO} \cdot 8\text{UO}_3 \cdot 3\text{P}_2\text{O}_5]$	A. Schoep (26)
Lead uranyl phosphate	$\text{Pb}_2[\text{UO}_2(\text{PO}_4)_2]$	A. Schoep (26)
PARSONITE	$\text{Pb}_2[\text{UO}_2(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$	A. Schoep (26)
DUMONDITE	$[2\text{PbO} \cdot 3\text{UO}_3 \cdot \text{P}_2\text{O}_5] \cdot 5\text{H}_2\text{O}$	A. Schoep (26)
Lead uranyl phosphate monohydrate	$\text{Pb}_2[\text{UO}_2(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$	A. Schoep (26)
RENARDITE	$[\text{PbO} \cdot 4\text{UO}_3 \cdot \text{P}_2\text{O}_5] \cdot 9\text{H}_2\text{O}$	A. Schoep (26)
Manganese uranyl phosphate	$[\text{MnO} \cdot 4\text{UO}_3 \cdot \text{P}_2\text{O}_5] \cdot n\text{H}_2\text{O}$	A. Schoep (26)
FRITZSCHEITE	$[\text{MnO} \cdot 4\text{UO}_3 \cdot \text{P}_2\text{O}_5] \cdot n\text{H}_2\text{O}$	A. Breithaupt (27)
Silver uranyl hexametaphosphate	$\text{Ag}_4[\text{UO}_2(\text{PO}_3)_6]$	P. Pascal (28)
Barium uranyl hexametaphosphate	$\text{Ba}_4[\text{UO}_2(\text{PO}_3)_6]$	P. Pascal (28)
Uranium phospho- decachloride	$[\text{UCl}_5 \cdot \text{PCl}_5]$	A. Cronander (29)
Uranous tetra- chlorophosphate	$[\text{U}_3(\text{PO}_4)_4\text{UCl}_4]$	A. Cronander (29)
Uranous tetrachloro- hydrophosphate	$[\text{U}(\text{HPO}_4)_4\text{UCl}_4]$	J. Aloy (30)
Uranyl nitratophosphate	$[2\text{UO}_3 \cdot \text{U}_2\text{O}_5 \cdot \text{P}_2\text{O}_5] \cdot 16\text{H}_2\text{O}$	W. Heintz (31)

Note: the literature cited will be found at the end of this chapter.

Uranyl hypophosphite, $[\text{UO}_2(\text{H}_2\text{PO}_2)_2] \cdot \text{H}_2\text{O}$, is a crystalline powder obtained when ammonium diuranate and hypophosphorous acid are digested together. The substance is insoluble in water but soluble in acids. It decomposes with explosive violence at temperatures, a peculiarity which has not been studied thoroughly. By the action of alkali phosphates on uranyl hypophosphite a series of complex salts is formed:



with the known representative having $R = \text{Na}$ and $n = 3\frac{1}{2}$ or 5. Another related series is better represented:



with the members having $R = \text{NH}_4$, K , and Na ; and, $n = 4\frac{1}{2}$ or 6.

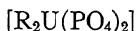
By the action of phosphorus trichloride on ammonium diuranate uranyl phosphite, $[(\text{UO}_2)_3 \cdot \text{H}_6(\text{PO}_3)_4] \cdot 12\text{H}_2\text{O}$ is produced.

A number of uranous phosphates are known, e.g., an acidic and a basic salt $[\text{UO}_2\text{P}_2\text{O}_5] \cdot \text{H}_2\text{O}$ and $[2\text{UO}_2 \cdot \text{P}_2\text{O}_5]$, respectively. Also, an ortho and a meta salt: $\text{U}_3(\text{PO}_4)_4$ and $\text{U}(\text{PO}_3)_4$, as well as a pyro salt: UP_2O_7 . Uranous chlorophosphate suggests a series:



with the known compound having $\text{X} = \text{Cl}$. Perhaps other halogens may complete the series.

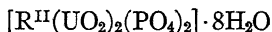
Fusion of alkali metaphosphates with uranyl salts in an atmosphere of carbon dioxide produces:



where $R = \text{Na}$, K , or $\text{R}_2 = \text{Ca}$, Sr , or Ba .

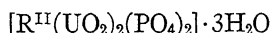
Compounds as simple as uranyl phosphate exist in nature. One of these is *uranospathite* which contains water of hydration. Uranyl metaphosphate is $\text{UO}_2(\text{PO}_3)_2$, while uranyl orthophosphate is $(\text{UO}_2)_3(\text{PO}_4)_2$. The latter compound may be modified further to two hydrogen-containing compounds. In one, UO_2HPO_4 , no water of hydration is present while in the other, $\text{UO}_2(\text{H}_2\text{PO}_4)_2$, three molecules of water of hydration are present. Uranyl pyrophosphate exists, its formula being $(\text{UO}_2)_2\text{P}_2\text{O}_7$.

Most important is the double salt series:

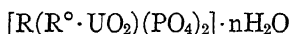


with well known mineral species and artificially prepared compounds as follows: R = Ca(*autunite*); Ba(*uranocircite*); Cu(*chalcocite*); 2K(no H₂O); and, 2NH₄(3H₂O).

Dewindite is a double salt: [Pb(UO₂)₂·(PO₄)₂]·3H₂O, the series being:



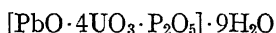
which exists in two modifications, the second being *stasite*. *Stasite* is: [4PbO·8UO₃·3P₂O₅]·12H₂O. The replacement of one uranyl group by lead (R) leads to a second series:



$$n = 1$$

when both R and R[°] are lead the substance is known as *parsonite*.

Renardite is another compound of this sort, a lead uranyl phosphate with the structure:



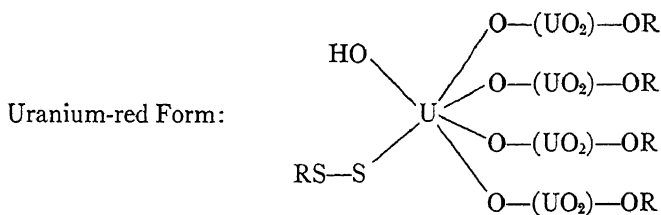
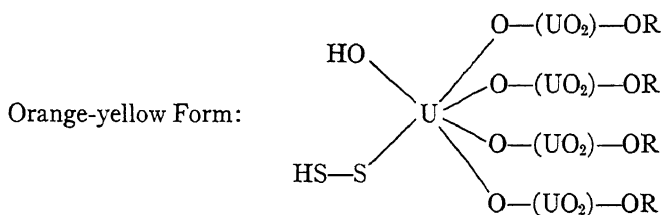
while *uranocircite* is the hydrated barium uranyl phosphate described above.

Uranium Sulfates

The compounds of uranium and sulfur are many. Non-oxygenated salts, e.g., sulfides are of three kinds: US, uranium monosulfide, which consists of a black powder; U₂S₃, uranium sesquisulfide, which consists of a grey-black needle-like material; and, US₂, uranium disulfide, which may be prepared by heating a mixture of uranium metal with sulfur at 500° C. A hydrated form of the latter is also known, being obtained by precipitation from uranous solutions with alkaline sulfides. An oxysulfide of uranium, [U₃O₂S₄] is also known. This substance can be prepared by heating uranium oxide with ammonium chloride and sulfur.

A sulfide of considerable interest is uranyl sulfide, UO_2S . Uranyl sulfide may be obtained as a result of the reaction between an alcoholic solution containing a uranyl salt and a soluble sulfide. Köhlschütter (1901) has drawn attention to the complexity of substances which are formed when uranyl sulfide is digested for several days in an excess of ammonium sulfide in the air. The result of the reaction is a red complex known as uranium red. This substance is a member of a series formed by the reduction of solutions of alkali uranates which contain an excess of uranyl sulfate and a free base by hydrogen sulfide. The first complex formed in these reactions is an orange-yellow material which appears to have the structure: $[\text{5UO}_3 \cdot 2\text{K}_2\text{O} \cdot \text{H}_2\text{S}_2]$.

On addition of an alkali uranium-red is formed and this appears to have the composition: $[5\text{UO}_3 \cdot 2\text{R}_2\text{O} \cdot \text{HRS}]$, where R is usually K. Köhlschütter suggested the following constitutions for these complexes:

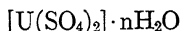


Uranium sulfites are known, these leading to more complex uranyl sulfites:

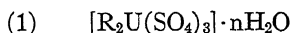


with $R = Na, NH_4$, or K and $x = 1$ to 4 , and $y = 1$ to 5 . It will be noted that the entire complement of complex uranyl sulfites is not worked out.

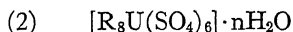
The lowest uranium sulfate is exemplified by:



this compound also being known as uranous sulfate. In salts now known n may have any value from 1 to 9 although only those salts with $n = 2, 4, 8$, or 9 are stable. Isomorphous with hydrated thorium sulfates are the uranous sulfates with $n = 4, 8$, or 9 . Uranous sulfate also forms double salts of two kinds:



and,



In double salts of this type now described (1) contains $R = K$ and $n = 2$ while (2) contains $R = NH_4$ and $n = 3$. Doubtless further investigations will reveal higher members in the series.

Uranium dithionates are known with the following structure:

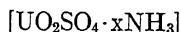


with the salts having $x = 6, 7$, or 8 and $n = 10, 8$, or 21 , respectively. Two other uranium compounds are the pyrosulfate, $UO_2S_2O_7$ and the thiosulfate, $UO_2S_2O_3$.

Oxygenated compounds of uranium in the hexavalent state are those which involve the uranyl radical. Uranyl sulfate, UO_2SO_4 , consists of green-yellow prismatic crystals which

are stable in diffused light but are reduced by strong radiation of wavelengths which may range between 0.01, e.g., gamma radiation, and 8000 A.U., e.g., red and lower infra-red radiation. Reduction occurs greatly in intense ultraviolet radiation.

Two kinds of acid-uranyl sulfate are known: $[\text{UO}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4]$ and $[2\text{UO}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4] \cdot 5\text{H}_2\text{O}$. Likewise, two forms of basic-uranyl sulfate have been recognized: $[3\text{U}_2\text{O}_3 \cdot \text{SO}_3] \cdot 2\text{H}_2\text{O}$ and $[4\text{U}_2\text{O}_3 \cdot \text{SO}_3] \cdot 7\text{H}_2\text{O}$. Addition compounds are formed when ammonium hydroxide or ammonia is added to uranyl sulfate:



with $x = 2, 3$, or 4 (cf. with ammino compounds and also with the salt discussed under hexavalency in the section on valency). In 1909 von Unruh pointed out that the depth of green color of these salts increases with the NH_3 content, being the greatest for the $x = 3$ salt.

Several complex uranyl sulfates are known:

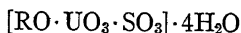


where $\text{R} = \text{NH}_4, \text{K}$, or Rb . Also,



where $\text{R} = \text{NH}_4, \text{Cs}, \text{Na}, \text{K}$, or Tl . Similar salts are known for lithium (with $4\text{H}_2\text{O}$) and for magnesium (with $5\text{H}_2\text{O}$).

Gilpinite, chemically represents a series of double sulfates:



with $\text{R} = \text{Cu}, \text{Fe}$, or 2Na . *Gilpinite* is also known as *johannite*. *Uranopilite* is a naturally occurring compound of this sort, being a hydrated calcium uranyl sulfate.

Zippeite is less complex than the above minerals and is a hydrated uranyl sulfate formed by weathering of primary uranium minerals.

URANIUM SULFATES

<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Uranium hydro- disulfate.....	$[\text{UH}(\text{SO}_4)_2]$	A. Rosenheim (1)
Uranous oxysulfate dihydrate.....	$[\text{UO}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$	E. Peligot (2)
Uranous oxysulfate octahydrate.....	$[\text{UO}(\text{SO}_4)] \cdot 8\text{H}_2\text{O}$	J. Ebelmen (3)
Uranous hexoxytetra- sulfate.....	$[\text{U}_5\text{O}_6(\text{SO}_4)_4] \cdot 18\text{H}_2\text{O}$	F. deConinck (4)
Uranous dihydro- pentasulfate.....	$[\text{U}_2\text{H}_2(\text{SO}_4)_5]$	V. Köhlschutter (5)
Uranous dihydro- trisulfate.....	$[\text{U}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4]$	F. Giolitti (6)
Ammonium uranous tetrasulfate.....	$[(\text{NH}_4)_4\text{U}(\text{SO}_4)_4]$	C. Rammelsberg (7)
Ammonium uranous hexasulfate.....	$[(\text{NH}_4)_6\text{U}(\text{SO}_4)_6]$	V. Köhlschutter (5)
Potassium uranous trisulfate.....	$[\text{K}_2\text{U}(\text{SO}_4)_3] \cdot \text{H}_2\text{O}$	C. Rammelsberg (7)
Uranyl sulfate.....	$[\text{UO}_2(\text{SO}_4)]$	J. Ebelmen (8)
Uranyl sulfate monohydrate.....	$[\text{UO}_2(\text{SO}_4)] \cdot \text{H}_2\text{O}$	H. Lescoeur (9)
Uranyl sulfate trihydrate.....	$[\text{UO}_2(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$	J. Ebelmen (8)
Uranyl trioxysulfate.....	$[(\text{UO}_2)_4\text{O}_3\text{SO}_4]$	N. Athanasesco (10)
Uranyl dioxysulfate.....	$[(\text{UO}_2)_3\text{O}_2\text{SO}_4]$	J. Ordway (11)
Uranyl dioxysulfate dihydrate.....	$[(\text{UO}_2)_3\text{O}_2\text{SO}_4] \cdot 2\text{H}_2\text{O}$	N. Athanasesco (10)
Uranyl dioxysulfate tetradecahydrate.....	$[(\text{UO}_2)_3\text{O}_2\text{SO}_4] \cdot 14\text{H}_2\text{O}$	J. Vogl (12)
URACONITE.....	$[(\text{UO}_2)_3\text{O}_2\text{SO}_4] \cdot 15\text{H}_2\text{O}$	J. Vogl (12)
Uranyl oxysulfate.....	$[(\text{UO}_2)_2\text{OSO}_4] \cdot n\text{H}_2\text{O}$	J. Ordway (11)
JOHANNITE.....	J. John (13)
GILPINITE.....	$[(\text{R}^{\text{II}})\text{O} \cdot \text{UO}_3 \cdot \text{SO}_3] \cdot 4\text{H}_2\text{O}$	E. Larsen (14)
		Cf. John (13)
ZIPPEITE.....	W. Haidinger (15)
VOGLIANITE.....	J. Vogl (16)
Uranyl dihydro- trisulfate.....	$[2(\text{UO}_2)\text{SO}_4 \cdot \text{H}_2\text{SO}_4]$	G. Wyrouboff (17)
Uranyl dihydrosulfate...	$[(\text{UO}_2)_2(\text{SO}_4)_2\text{H}_2(\text{HSO}_4)_2]$...	Schultz-Sellak (18)
Uranyl triammino- sulfate.....	$[\text{UO}_2(\text{SO}_4) \cdot 3\text{NH}_3]$	A. von Unruh (19)

URANIUM SULFATES (*Continued*)

<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Uranyl diammino sulfate.....	$[\text{UO}_2(\text{SO}_4) \cdot 2\text{NH}_3]$	A. von Unruh (19)
Uranyl tetraammino-sulfate.....	$[\text{UO}_2(\text{SO}_4) \cdot 4\text{NH}_3]$	A. von Unruh (19)
Ammonium uranyl disulfate.....	$[(\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2]$	J. Arvedson (20)
Ammonium diuranyl trisulfate.....	$[(\text{NH}_4)_2(\text{UO}_2)_2(\text{SO}_4)_3]$	H. Bolton (21)
Ammonium diuranyl tri-sulfate dihydrate.....	—————	F. de Coninck (22)
Ammonium uranyl disulfate.....	$[(\text{NH}_4)_4\text{H}_2 \cdot \text{UO}_4(\text{SO}_4)_2]$	J. Meyer (23)
Ammonium potassium uranyl trisulfate.....	$[(\text{NH}_4)_2\text{K}_4 \cdot \text{UO}_3(\text{SO}_4)_3]$	J. Meyer (23)
Ammonium uranyl trisulfate.....	$[(\text{NH}_4)_4(\text{UO}_2)(\text{SO}_4)_3]$	E. Rimbach (24)
Potassium uranyl trisulfate.....	$[\text{K}_4(\text{UO}_2)(\text{SO}_4)_3]$	E. Rimbach (24)
Ammonium diuranyl trisulfate.....	$[(\text{NH}_4)_2(\text{UO}_2)_2(\text{SO}_4)_3]$	A. Colani (25)
Hydroxylamine diuranyl trisulfate...	$[(\text{NH}_4\text{O})_2\text{SO}_4 \cdot 2\text{UO}_2 \cdot \text{SO}_4]$	E. Rimbach (26)
Ethylenediamine uranyl disulfate.....	$[\text{C}_2\text{H}_6(\text{NH}_2)_2 \cdot \text{UO}_2(\text{SO}_4)_2]$	H. Grossman (27)
Guanidine uranyl disulfate.....	$[(\text{C}_6\text{H}_5\text{N}_3)_2 \cdot \text{H}_2\text{SO}_4 \cdot \text{UO}_2(\text{SO}_4)]$	G. Canneri (28)
Lithium uranyl disulfate.....	$[\text{Li}_2(\text{UO}_2)(\text{SO}_4)_2]$	F. de Coninck (29)
Sodium uranyl disulfate.....	$[\text{Na}_2(\text{UO}_2)(\text{SO}_4)_2]$	F. de Coninck (29)
Sodium uranyl trisulfate.....	$[\text{Na}_4(\text{UO}_2)(\text{SO}_4)_3]$	A. Colani (30)
Potassium uranyl disulfate.....	$[\text{K}_2(\text{UO}_2)(\text{SO}_4)_2]$	J. Berzelius (31)
Potassium uranyl disulfate trihydrate...	$[\text{K}_2(\text{UO}_2)(\text{SO}_4)_2] \cdot 3\text{H}_2\text{O}$	P. Groth (32)
Potassium uranyl trisulfate.....	$[\text{K}_4(\text{UO}_2)(\text{SO}_4)_3]$	E. Rimbach (33)
Potassium uranyl trisulfate pentahydrate.....	—————	A. Colani (34)
Potassium uranyl trisulfate hexahydrate.....	—————	J. Meyer (35)

URANIUM SULFATES (*Continued*)

<i>Name</i>	<i>Formula</i>	<i>Early Reference</i>
Potassium uranyl disulfate.	$[\text{K}_2(\text{UO}_2)(\text{SO}_4)_2]$	E. Rimbach (33)
Rubidium uranyl disulfate.	$[\text{Rb}_2(\text{UO}_2)(\text{SO}_4)_2]$	E. Rimbach (36)
Rubidium uranyl trisulfate.	$[\text{Rb}_4(\text{UO}_2)(\text{SO}_4)_3]$	E. Rimbach (36)
Cesium uranyl disulfate.	$[\text{Cs}_2(\text{UO}_2)(\text{SO}_4)_2]$	F. de Coninck (37)
Calcium uranyl sulfate.	J. Smith (38)
MEDJIDITE.	J. Smith (38)
URANOCHALCITE.	A. Breithaupt (39)
URANOPILITE.	$[\text{CaO} \cdot 8\text{UO}_3 \cdot 2\text{SO}_3] \cdot 25\text{H}_2\text{O}$	A. Weisbach (40)
Magnesium uranyl disulfate.	$[\text{Mg}(\text{UO}_2)(\text{SO}_4)_2]$	F. de Coninck (41)
Thallous uranyl disulfate.	$[\text{Tl}_2(\text{UO}_2)(\text{SO}_4)_2]$	M. Kohn (42)

Note: the literature cited will be found at the end of this chapter.

Uranium Combined with Other Elements

A pyrophoric material containing uranium and *arsenic* is uranium arsenide, U_3As . Higher compounds of this sort are uranous metaarsenite, $\text{UO}_2(\text{AsO}_2)_2$, and uranous arsenate, $[\text{UH}(\text{AsO}_4)_2] \cdot n\text{H}_2\text{O}$, where $n = 2$ or 4.

Trögerite, a naturally occurring radioactive mineral with the formula $[(\text{UO}_2)_3(\text{AsO}_4)_2] \cdot 12\text{H}_2\text{O}$ is uranyl orthoarsenate. Trögerite may also be prepared artificially, a fact of interest to those who require large amounts of rare secondary uraniferous minerals for studies which are independent of natural sources.

Two acid arsenates exist. One is uranyl monohydrogen arsenate with the composition: $[\text{UO}_2 \cdot \text{HAsO}_4] \cdot 4\text{H}_2\text{O}$. The other is uranyl dihydrogen arsenate: $[\text{UO}_2(\text{H}_2\text{AsO}_4)_2] \cdot 3\text{H}_2\text{O}$. By heat treatment of these uranyl pyroarsenate: $[(\text{UO}_2)_2\text{As}_2\text{O}_7]$, is obtained.

Complex uranyl arsenates are important because they exist

in nature in a variety of modifications. *Zeunerite* is a copper ($R = \text{Cu}$) uranyl arsenate with the structure :



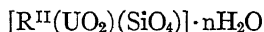
whereas *uranospinite* is calcium uranyl arsenate with the same structure ($R = \text{Ca}$). Related to these is a series of lower compounds :



where $R = \text{NH}_4$ or K and $n = 3$ or 5 . Basic bismuth uranyl arsenate occurs in nature as *walpurkite*.

A stable and highly acid resisting material is uranium silicide, USi_2 . This compound may be obtained by the Goldschmidt Reaction involving reduction by aluminum. The procedure is to heat a mixture of urano-uranic oxide, silicon dioxide, aluminum powder, and sulfur together until the reaction is complete. An oxygenated salt involving uranium and *silicon* is uranyl silicate, this being the basis for the hydrated silicates which occur in nature as *gummite*, *uranophane*, *uranotil*, and others which include alkali-earth elements, e.g., hydrated calcium uranyl silicate. A uranium silicofluoride is known, this substance being soluble in water.

Kasolite is lead uranyl silicate, the series being :



the singular representative of the series is kasolite, $R = \text{Pb}$.

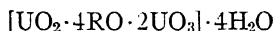
Skłodowskite is a compound of this sort : $[\text{MgO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2] \cdot 7\text{H}_2\text{O}$. A simple uranium silicate is *soddite* (sodylite) :



Naturally occurring substances which involve *thorium* and uranium have two important forms. The two forms of thorouraninities are :



as illustrated by *bröggerite* and,



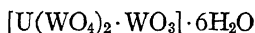
as illustrated by *cleveite*.

Miexner (1940) studied non-luminescent uranium minerals and found them be micas and silicates of composition:

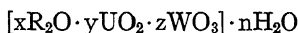


where R = Cu, Fe, Pb, Bi, Mn, or UO_2 , and X = P, As, V, or S. There are a number of others of this class, among them being *cuprosklodowskite*: $[\text{CuO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2] \cdot 6\text{H}_2\text{O}$.

In 1843 Rammelsberg prepared compounds between uranium and *tungsten*. When uranium tetrachloride is added to solutions of ammonium tungstate an X-ray fluorescent substance is obtained:

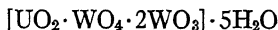


Complex uranyl tungstates may be prepared by the addition of uranium sulfate to alkaline paratungstates, the reaction producing:

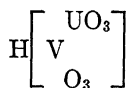


with only a small number of members of the series having been prepared: $\text{x} = 12(\text{Na}), 9(\text{K}), \text{NH}_4$, and $\text{y} = 6(\text{Na}), 6(\text{K})$, and $\text{z} = 8(\text{Na}), 8(\text{K})$; and, $\text{n} = 25(\text{Na})$ and $34(\text{K})$.

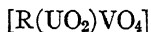
Uranyl tungstate, UO_2WO_4 , has a more complex homolog which is lower than its first mentioned analog:



The uranyl radical unites with the *vanadate* radical. The result may be regarded as being derived from uranyl vanadic acid which has the structure:



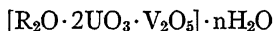
By adding uranium dioxide (uranic anhydride) to fused potassium or sodium metavanadate microscopic, rectangular, fluorescent plates of the following composition are obtained:



R = Na or K

Probably the derivatives of a relatively stable uranyl vanadic acid are analogs to uranyl phosphate which occurs naturally in a number of minerals, e.g., autunite, bassettite, and others.

Uvanite is a hydrated uranyl vanadate. An important series of double salts containing both uranium and vanadium exist:



with the most important representative being *carnotite*, R = K (n = 3). Another is *rauvite*, calcium uranyl vanadate, $[CaO \cdot 2UO_3 \cdot 6V_2O_5] \cdot 2H_2O$. *Tyuyamunite* is a hydrated calcium uranyl vanadate of composition similar to *rauvite*: $[CaO \cdot 2UO_3 \cdot V_2O_5] \cdot nH_2O$.

Compounds exist between *selenium* and uranium. The simplest of these is probably uranium sesquiselenide, U_2Se_3 , first prepared by Colani in 1903. The method of preparation for uranium sesquiselenide consists of passing a mixture of hydrogen and selenium vapor over $Na_2U_4Cl_6$ at $1000^\circ C$. Another selenide is uranium selenide, USe_2 , which may be prepared by fusion of double uranyl chlorides with metallic selenides at high temperatures.

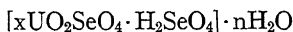
The simplest oxygenated uranium and selenium compound is uranyl selenide, UO_2Se , which may be prepared by fusing selenium with a mixture of potassium cyanide and U_3O_8 at red heat, the resulting compound being stable but readily decomposed by acids. Uranyl selenite, UO_2SeO_3 , is a lemon-yellow substance prepared by precipitation from solutions

containing uranyl ions with sodium selenite. Complex uranyl selenites were prepared first in 1879 by Boutzoureano :

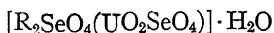


with known members having $x = 1, 2$, or 3 ; $y = 2, 3$, or 5 ; and $n = 1, 7$, or 9 . They are obtained by the reaction of alkali selenites on uranyl salts.

In addition to this series of selenium complexes a uranyl selenate series is known :



the members now known to belong to this series have $x = 1$ or 2 and $n = 12$ or 18 . These compounds lead to the double selenates :



with members consisting of $\text{R} = \text{K}$ and NH_4 .

Few compounds have been described between uranium and *tellurium*, viz., uranium telluride, U_2Te_2 ; uranyl tellurate, UO_2TeO_4 ; and a compound prepared by the present writers, uranyl tellurite, UO_2TeO_3 , a pale yellow substance.

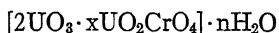
By subjecting a mixture of uranium metal and boron to the heat of a vacuum electric furnace a compound may be formed which consists of uranous boride, UB_2 . Other compounds of boron and uranium exist. Uranyl borate, and the uranyl borotungstate, as well as uranous perborate, UBO_4 .

Few compounds have been prepared which involve both uranium and *antimony*. Probably the most well-known is uranous antimonate, U_3Sb_4 .

The addition of potassium chromate solutions to uranyl salts produces an effluorescent substance called uranyl chromate, $[\text{UO}_2\text{CrO}_4] \cdot 3\text{H}_2\text{O}$. Of this salt two basic forms are known :



and,

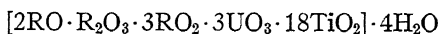


with known compounds having $x = 1$ or 2 and $n = 6$ or 8 . When alkali uranates are heated with chromic acid and evaporated a complex series of uranyl chromates is evolved:



where $R = K, NH_4$, and Na ; $n = 6$ or 10 .

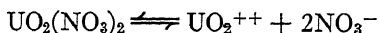
Complex compounds involving *titanium* and uranium exist, one of the few compounds being represented by:



the substance occurring naturally as *brannerite*, where the valences of element $R = 2, 3$, and 4 .

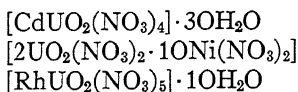
In 1907 Laucein prepared compounds containing both uranium and *molybdenum*, one of which is uranyl molybdate, UO_2MoO_4 forming, on reduction, uranium molybdate, $U(MoO_4)_2$. Two other molybdenum-uranium salts are known: uranium paramolybdate, $[3UO_3 \cdot 7MoO_3]$; and, uranyl octamolybdate, $[UO_3 \cdot 8MoO_3] \cdot 13H_2O$. It seems apparent that either or both of these lead to complex series although this remains to be demonstrated experimentally. *Uranomolybdate*, uranium trimolybdate, is a salt found in nature.

The nitride of uranium has already been discussed. Urinous nitrate is a compound which forms unstable green solutions and which introduces the important uranyl nitrate, $[UO_2(NO_3)_2] \cdot 6H_2O$. Uranyl nitrate is a yellow solid which is highly fluorescent and when obtained commercially usually contains small amounts of alkali as impurities. Its density is 2.807 and it melts at $60.2^\circ C$. and boils at $118^\circ C$. The crystals are deliquescent and soluble in both water and many organic liquids. It was shown by Gomez in 1919 that uranyl nitrate dissociates into uranyl ions and nitrate ions:



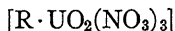
Uranyl nitrate usually has six molecules of water of hydration although salts have been prepared from $[\text{UO}_2(\text{NO}_3)_2] \cdot n\text{H}_2\text{O}$ with $n = 0, 1, 2, 3, 4, 6$, and 24.

Complex unstable double salts of uranyl nitrate are known. These were described in 1912 by Laucein, i.e.,



An ethylenediamine salt is: $[\text{C}_2\text{H}_4(\text{NH}_4)_2 \cdot 2\text{HNO}_3 \cdot \text{UO}_2(\text{NO}_3)_2]$.

Complex double salts are known with the composition:

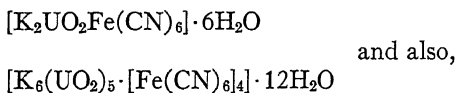


and the now-known compounds have $\text{R} = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$, and Tl . These were prepared in 1903 by Myer and Wendel who obtained the crystalline precipitates formed after mixing solutions of the metals in nitric acid.

It appears that both uranous cyanide and uranyl cyanide have not been prepared since efforts by the usual reactions merely yield hydrocyanic acid and the hydroxide, or a double salt:



Of greater interest, especially to the analyst, is the double uranyl ferrocyanide. The compound typifies a series:



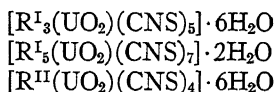
Of a related nature is uranyl platinocyanide, a non-fluorescent salt.

When potassium cyanate solutions are added to uranyl salts a compound known as uranyl cyanate, $\text{UO}_2(\text{CNO})_2$, is formed. On hydrolysis uranyl cyanate is thought to yield

an orange-yellow complex: $[(\text{UO}_2)_2(\text{CNO})_5]\text{K}$ or, if an excess of cyanate is present golden-yellow crystals of another complex will form: $[\text{UO}_2(\text{CNO})_3]\text{K}$.

Uranyl thiocyanate, $[\text{UO}_2(\text{CNS})_2] \cdot 8\text{H}_2\text{O}$ is a red substance formed when solutions of thiocyanate ions are added to uranyl salts. The addition of pyridine to uranyl thiocyanate forms a basic complex which has been described previously.

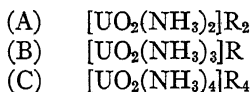
Uranyl thiocyanate leads to complexes, all of which dissociate into simple ions, the compounds being represented by:



as would be expected these are obtained when alkali thiocyanate solutions are added to uranyl thiocyanate solutions.

Ammino Derivatives

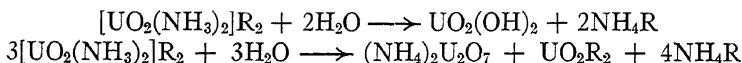
The ammino derivatives of uranium have been described by M. M. J. Sutherland (1928) and others. Most of the compounds are of the uranyl ammino type and are capable of uniting with ammonia gas, if dry, to form yellow amorphous powdery substances of the following general structure:



The tetraammino compounds (C) lose ammonia at ordinary temperatures to form triammino compounds (B); these in turn being converted into diammino compounds (A) on slight warning. The final product in this is uranium dioxide and an ammonium salt.

In cold water diammino uranyl compounds decompose with the precipitation of yellow hydroxides and on boiling

the filtrate an almost colorless liquid is obtained. This contains a small amount of uranium:



Liquid ammonia transforms diammino or triammino uranyl compounds into the tetraammino product which exists only below 5° C. When the temperature is raised decomposition occurs with the formation of uranium dioxide and ammonium salts (re. previous equation). The uranyl ammino salts unite readily with ether forming compounds which may be compared to hydration (Gmelin and Kraut, 1912).

When an aqueous solution of phosphoric acid is saturated with an amine and this solution is added to a uranyl salt drop by drop a complex amminophosphate is obtained:



where compounds with $\text{R} = \text{CH}_3 \cdot \text{NH}_2$; $\text{C}_2\text{H}_5 \cdot \text{NH}_2$; and, $(\text{CH}_3)_3 \cdot \text{N}$ were prepared by Barthe in 1911.

It is interesting to compare the ammino compounds of uranium, and their chemistry, with the section on amines as precipitants in uranium analysis in a following chapter.

In writing the chemical formulae for many of the foregoing substances it has been difficult, on the basis of present evidence, to attach H_2O as a hydrate or include it in the structure to form an aqua salt. The hydrate notation generally has been preferred although doubtless the latter condition exists in these compounds.

Organo-Uranium Compounds

It may appear that detailed description of remote organo-uranium compounds is of incidental importance. But far

from being anything of the sort are such details since the basis for many of the much needed sensitive tests for uranium will doubtless someday depend upon compounds of uranium which involve organic addenda.

As would be expected, tests for uranium by organic substances depend on the enhancement of reactivity in the several ways possible. The reactivity of elements may be raised by the formation of complexes, e.g., with 1, 2-dihydroxyanthraquinone. Increased reactivity is often accomplished by shifting the equilibrium of a system through the removal of a reaction product to form a complex. It is possible to increase the dissociation equilibrium of a weak electrolyte by incorporating it in a complex combination. Then, under certain conditions, the concentration of one particular ion is so greatly raised that reaction, not shown by the original compounds because of below-threshold of detection dissociation, becomes possible.

An increase in reaction velocity of slow reactions without alteration of equilibrium may be brought about by catalysis. Examples of accelerated reactions due to the presence of small amounts of specific materials are well known. The approach to an effective mode of uranometry by catalysis, inducement or acceleration, has been studied mainly from a photochemical standpoint although other aspects yet remain relatively obscure.

Of the same nature is induced precipitation and induced solution caused by mechanisms probably closely related to the above. In induced precipitations the precipitate contains accompanying substances which do not react appreciably with the precipitate and which cause solubility anomalies of the constituents of the precipitate. Likewise, a similar action occurs on solution of materials. Some insoluble materials are brought into solution when these attendant materials are

present. This approach to uranometry has been studied only scantily.

Concerning organo-uranium compounds it will be noted that sometimes it has been difficult to effectively interpret structure. The same condition, as is well known, exists with minerals which involve highly intricate naturally formed inorganic compounds of uranium. A number of salts are known that can be regarded as combinations (aggregations or solvates) of molecules which are ordinarily stable by themselves. In certain salts the formulation of structure is by joining of the principal valences of the atoms, this appearing to be the simplest explanation for structure.

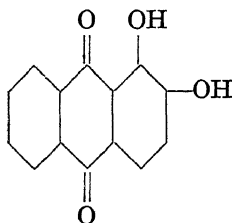
But in these same salts it sometimes is necessary to assume that the so-termed saturated compounds still possess additional combining power, the true nature of which is not known at present with certainty. This additional combining power finds its expression in the formation of complex compounds, the action being known as co-valency. So it is with this in mind that assumption of an additional combining capacity takes on added import. This import is in correct prediction of the behavior of these compounds and the resulting benefits analytical chemistry derives from them (cf. Feigl, 1940).

An analytical approach to the most suitable organic reagent has been given by Feigl, as regards metallic ions, this holding true to a certain degree for the uranyl ion. In addition to the production of inner complexes salt-formation resulting in the union of the uranyl ion (or, tetravalent uranium ion) with certain organic groups yields normal salts which are often characteristic of the ion which is involved. These salt-forming groups, when present on a multitude of different aromatic or aliphatic structures obviously present a wide range of number and sort of possibilities. Prominent among these groups are the following:

SO ₃ H.....	Sulfonic
SO ₂ H.....	Sulfinic
COOH.....	Carboxyl
OH.....	Hydroxyl
SH.....	Sulfhydryl
NOH.....	Oxime
NH.....	Imide; See the section on amines as precipitants.

According to Feigl, the structure of the reagent will disclose the capability of producing inner complex compounds. The requirements include one or more of the acid groups listed above together with an atom (uranium) capable of developing co-valent linkages in such proximity to an acid (mobile) hydrogen atom that there is possibility of a ring closure (five or six membered, or multiples if fluorescence is an important aspect) through participation of principal and auxiliary valences. Generally, attention should be directed to the O, S, or N atoms in the CO, CS, NH₂, NHR, NR, R₂, NO, NO₂, and double-bonded N or double-bonded C in either open or closed chains.

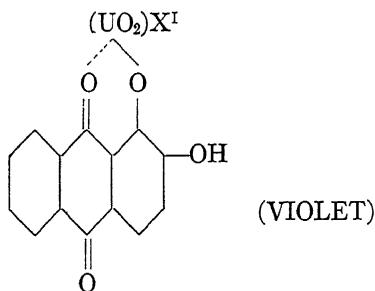
Hydroanthraquinones such as alizarin which have a hydroxyl group in the alpha position :



1, 2, dihydroxyanthraquinone

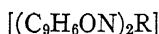
can form inner complex compounds with metal salts as well as with acids. Feigl has described this mechanism (1940)

and compounds such as that with SnCl_4 have been prepared by Pfeiffer (1913). With uranyl salts the structure may be regarded as:

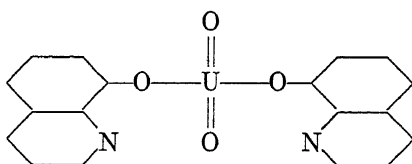


Uranyl lake of
Hydroxyanthraquinone

Probably one of the most interesting organo-uranium compounds is that with 8-hydroxyquinoline. Oxine (8-hydroxyquinoline) forms a number of insoluble compounds of the following type:

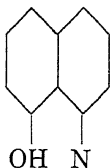


where R is a bivalent metal or radical, e.g., UO_2^{++} . These salts are characterized by definite construction, stability, and crystalline form. The uranyl salt of 8-hydroxyquinoline is precipitated from uranyl salts in solution. Uranyl 8-hydroxyquinolate has the following structure:

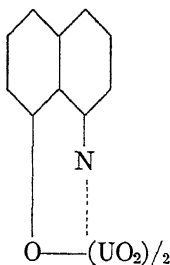


The precipitation occurs without water of crystallization. One molecule of 8-hydroxyquinoline is lost, however, on heating the complex to 200° C. (F. Frere, 1933).

The 8-hydroxyquinolinate has been interpreted on other bases. Feigl, and others, have indicated that the cyclic bound nitrogen atoms in the phenol portion of the compound participate to form inner complex salts. The reagent itself has the following structure:

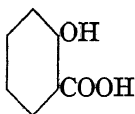


The inner complex of hydroxyquinoline might then be:

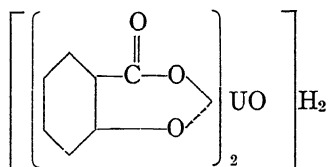


with $\frac{(UO_2)}{2}$ possibly being $\frac{U}{4}$ (cf. data on other salts of this sort) instead, present evidence being in favor of the former ion. F. Hahn and K. Vieweg (1926) and R. Berg (1935) used these reagents for the detection, determination, and separation of metals.

Salicylic acid has the following constitution:

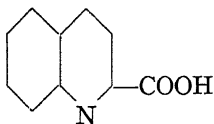


and when this aromatic acid comes in contact with uranium a soluble inner complex with an orange-red color is probably formed :

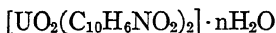


This structure is based on the data of Muller (1919) (re. next chapter) which states that uranyl ions form the salt. On the basis of other uranium salts of the inner complex type, e.g., the catechol compound described by Rosenheim, et al, in 1931, it may be that UO_2^{++} would be replaced by U^{4+} , the values for H and the organic addenda then doubling.

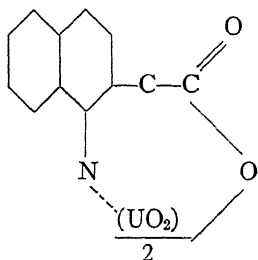
Quinaldic acid forms inner complexes which are soluble, the reagent having the structure :



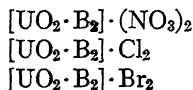
and is prepared by solution in sodium hydroxide or ammonium hydroxide, this on addition to uranyl ions forms golden insoluble amorphous precipitates which are soluble in acids, according to data by Hopkins and Williams, Ltd., 1938. This source ascribed the composition of the quinaldic salt with the uranyl ion as :



On the other hand, Feigl (1940) stated that the result of coordination with a bivalent ion is a five membered ring with the nitrogen atom and the carboxyl group in the following position :

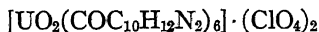


The complexes of uranium with bromo-antipyrine and nitroso groups were prepared by R. Rascanu in 1933. These may have value in analysis since on the basis of theory alone they would appear to be fluorescent, a fact which may be of further value in tests for uranium. All the salts prepared by Rascanu are decomposed by boiling water and as would be expected those with hexavalent uranium (UO_2) are the most stable. The compounds prepared are: $[\text{UO}_2(\text{NO})_4] \cdot (\text{NO}_3)_2$, and three bromo-antipyrines:



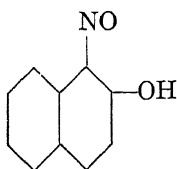
where B = bromo-antipyrine.

Another complex consisting of a double salt of the uranyl group with antipyrine has been prepared (cf. work of Rascanu on the bromo-antipyrine derivatives of UO_2 above). The salt:

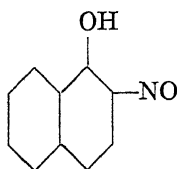


is produced on shaking a solution containing UO_2 , antipyrine, and ammonium perchlorate. The substance melts at 194 to 196° C. and decomposes at 270° C. At room temperature (20° C.) 0.46 gram of the complex will dissolve in 100 cc. of water. Analogs exist with Cl or NO_3 groups replacing the UO_2 .

Alpha-nitroso-beta-naphthol is a reagent which may be used for the determination of uranium. The substance has the structure :

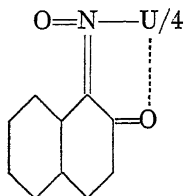


whereas the beta-nitroso-alpha-naphthol has the structure :



These form slightly soluble colored complex salts with heavy metals. The cobalt salt, first isolated in 1884 by Ilinski and von Knorre, is obtained in tautomeric quinoxime forms. Only the quinone oxime form can produce a salt although in concentrated acid solutions the phenol form is predominant. This explains the incomplete production of the cobaltic salt which, once formed, is insoluble in acids.

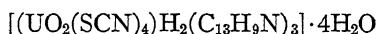
In studies by J. De Ment (1941)* results indicated that the uranium complex was probably obtained, with the following structure being likely :



* Unpublished.

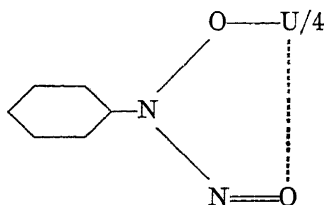
The salt is a dark rust brown semi-soluble material with properties common to others of this series. Its importance lies in its applications to the analytic determination of uranium.

Acridine forms complexes with a number of elements among them being uranium in the form of the sexvalent element (UO_2). Uranyl ions form insoluble precipitates of the acridine thiocyanate complex type:



The uranyl acridine thiocyanate complex exists as small light yellow spherules. When used as a test for uranium as little as 2 gamma of UO_2 may be detected (see chapter on analysis). Likely this complex is highly fluorescent since both UO_2 and acridine compounds are ordinarily intensely fluorescent. Other elements which form this complex are Cu, Fe, Co, Zn, Hg, Cd, Bi, and perhaps a few others (A. Langer, 1938).

Uranium, as well as copper, iron, and other elements, form salts with cupferron (nitrosophenylhydroxylamine). These provide the basis for detection and/or measurement of uranium. The structure of the uranium salt of nitrosophenylhydroxylamine is an analog to the salts of the other metals being:



This is on the basis of data by Hillebrand and Lundell (1929) although $\frac{\text{U}}{4}$ might be instead/also $\frac{(\text{UO}_2)}{2}$. The $\frac{\text{U}}{4}$ salt is precipitated from acid solutions.

By mixing hot solutions of glycine anhydride with salts of heavy metals, e.g., uranyl salts, and evaporating to incipient crystals it is possible to obtain complexes of composition: $C_4H_6N_2O_2 \cdot UO_2(X)_2$, where X may be any one of a number of radicals. These complexes are insoluble in non-polar compounds but are soluble in water with separation into their components.

As a catalyst and source of organo-metallic uranium one or more of the uranium soaps may be useful. These substances have not been described in any detail before so in lieu of their relative inertness under certain conditions, and because of their color and also because of the slight radioactivity uranium soaps may find one or more applications.

Metallic soaps in general enjoy rather widespread usage in industry due to their unique gelling properties in oils and solvents; because of their insolubility in water; because of the catalytic action directly caused by their metal content; because of their intrinsic lubricant properties; and, finally because of their plasticizing characteristics. These properties, combined with the special nature of uranium indicate that developments in research, arts, and industry are forthcoming. Applications in uranometry for uranium soaps are indicated. Stable gels involving uranium which are absolutely anhydrous, i.e., void of water, may be prepared by organic solvents and uranium soap. Gels of this sort may be of special value in research.

Extraction of Uranium from Its Ores

The important sources for uranium are pitchblende and carnotite. Other minerals, such as the secondary uraninites, have been used from time to time as commercial sources for uranium but eventually their use was abandoned due to the limited amounts of mineral obtainable. A number of rare uranium minerals are known which would be excellent

sources for uranium since extraction would be a relatively simple process.

The early workers extracted uranium from pitchblende by digesting the mineral with nitric acid or aqua regia and evaporating to dryness. Hydrochloric acid was used to extract the soluble matter and arsenic, lead, and other elements, were precipitated by hydrogen sulfide. The filtrate obtained from this treatment was mixed with nitric acid and ammonium carbonate. The precipitates formed consist of the oxides of uranium, zinc, and cobalt. The zinc and cobalt oxides are separated from the uranium by the addition of cold dilute hydrochloric acid. As a result of this reaction the uranium oxide remains as an insoluble residue while the others pass off in solution.

The early method for extraction of uranium from pitchblende has been modified considerably. The present method consists of heat treatment before the action of chemicals is relied upon to separate the uranium from its constituents. The pitchblende is concentrated by the aid of hand-picking or gravity methods and is roasted in a reverberatory furnace to remove the volatile elements, e.g., arsenic and sulfur. Sodium carbonate or sodium sulfate is added to the roasted ore and the mixture is fused in the furnace.

In this treatment the uranium is changed into sodium uranate along with the formation of molybdates, vanadates, and tungstates, i.e., group six elements, and arsenates. These pass into solution when the cold material is extracted by water. The residue is the beginning point for the extraction of radium which, at present, is the primary course followed in processing, the uranium being obtained as a by-product.

The uranium solution is digested with sulfuric acid which reacts with the uranium compound to form uranyl sulfate. The excess acid is removed by evaporation and the residue is extracted with water. The residue consists mainly of sili-

con dioxide, lead sulfate, and basic bismuth sulfate and arsenate. The two extracts are treated with an excess of sodium carbonate to precipitate the basic carbonates of iron, aluminum, nickel, and cobalt. The uranium remains in solution.

The uranium-containing solution is boiled and the clear liquid neutralized with dilute sulfuric acid and boiled down until the sodium diuranate appears as a bright yellow precipitate. The use of ammonium salts instead of sodium salts in the processing of uranium is often preferred since ammonium diuranate is obtained and this can be calcined to U_3O_8 .

In order to obtain relatively pure uranyl salts from these fractions, e.g., uranyl nitrate, treatment with nitric acid follows. Or, the roasted ore may be dissolved in nitric acid and the solution evaporated to dryness. The residue is digested and the solution filtered and allowed to crystallize. Nitric acid is used in the digestion.

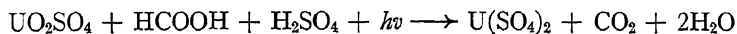
It is not usual for the phosphatic uranium minerals to be used as a commercial source for uranium. The extraction of uranium from these substances, as well as laboratory residues of this type, may be accomplished by the method of W. Jani (1871). The material containing uranium is heated with a reagent consisting of nitric acid and sulfuric acid. After solution has been completed the cold liquid is treated with sodium hydroxide and the precipitate formed washed with a solution of sodium carbonate. The filtrate is saturated with carbon dioxide and the uranium passes into solution from which it may be removed in the usual way.

Photochemical Aspects

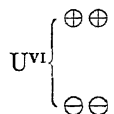
When light is absorbed by a solution of uranyl salt the uranyl ion may be considered to undergo a change from the "dark condition" to the "light condition." The light energy absorbed is later emitted as fluorescence. In the "light

condition" uranium is considered to be resolved by the displacement of electrons into a higher and a lower state of oxidation, the addition of another inhibiting substance being to destroy this condition.

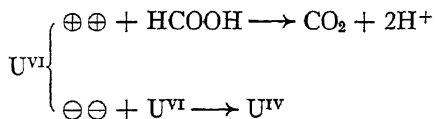
In the absence of an inhibitor the electron returns to its ground state and fluorescence occurs. For example, the photolysis of formic acid, catalyzed by uranyl sulfate:



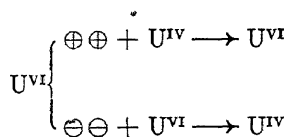
The uranyl compound, as hexavalent uranium is activated by light to a condition which has been represented by Bauer (1918) as:



The mechanism in the above reaction is promoted by:



This yield is diminished as photolysis proceeds and tetravalent uranium accumulates. Deactivation occurs according to:



Uranyl salts are of value in actinometry. This has been studied extensively by G. S. Forbes and others. For precision actinometry a solution of uranyl sulfate containing an excess

of oxalic acid has marked advantages being, according to Forbes, absence of dark reaction, great width of absorption band, zero order of light reaction, a temperature coefficient of about unity, and others.

In 1930 W. Leighton and G. Forbes redetermined the quantum yields for solutions of uranyl sulfate in oxalic acid which had been determined earlier by a number of investigators, e.g., Boll (1913) reported 50 molecules transformed per quantum for wave lengths of 2540 A.U.; Buchi (1924) 1.07 between 4000 and 4700 A.U.; Bowen and Watts (1926) 1.0 at wavelength 3130 A.U. and Anderson and Robinson (1925) 0.04 between 2000 and 4100 A.U.

The studies of 1930 indicated that the gross quantum yield, ϕ , at 25° C. for a solution of 0.01 M. uranyl sulfate and 0.05 M. oxalic acid varies between 0.60 at 2540 A.U. to 0.58 at 4350 A.U. with a minimum of 0.49 at 3660 A.U. These studies revealed values of about half those previously used for actinometry. The studies demonstrated another important fact. This consisted of the view that probably the photolyte is $\text{UO}_2\text{HC}_2\text{O}_4^+$ or $\text{UO}_2\text{C}_2\text{O}_4$, or some optical cluster equivalent (cf. Jones and Strong on solvates) to one of these and make it seem somewhat improbable that the photolysis depends mainly upon collisions of the second kind between uranyl and oxalate ions.

In 1934 G. Forbes and L. Heidt determined the optimum concentration of uranyl oxalate for use in actinometry. They found that an actinometer solution consisting of 0.01 M. uranyl sulfate and 0.05 M. oxalic acid, when diluted tenfold, remains constant within 3% in quantum yields at wave lengths 3130, 2800, 2540, and 2080 A.U., respectively.

Muller and his co-workers, West and Jette, in 1928, made a thorough investigation of the action of the uranyl ion as a photocatalyst. In the sensitized photochemical reaction the

energy absorbed from the incident radiation by the sensitizer is transferred to the reacting molecule in a collision of the second kind. Collisions of the second kind are those in which an excited atom loses a portion of its excitation energy during a collision.

As the sensitizing molecule is fluorescent, the fluorescence is quenched by the addition of the reacting substance. The uranyl ion either re-emits the absorbed energy as fluorescence or it effects the decomposition of the reactant, e.g., oxalic acid, by transferring the energy in a collision. There occurs, in a sense, competition, according to E. Hirschlaff,* between the photochemical decomposition and the quenching of fluorescence of the sensitizing ion.

The number of oxalic acid molecules, should this be the reactant, decomposed per quantum absorbed increases with the concentration. The probability of a collision becomes greater and attains unity at oxalic acid concentrations equal to that of the uranyl ions, indicating destruction of the photolyte complex mentioned previously.

A practical application of a reaction sensitized by fluorescing uranyl ions is the sensitizing of a photographic plate for the ultraviolet regions. The gelatine comprising the photographic emulsion absorbs the ultraviolet radiation so strongly that it renders the plate insensitive to this light; therefore, the radiation cannot penetrate into the emulsion and affect the silver salt. A layer of fluorescent uranium molecules placed on the plate absorbs the ultraviolet rays and re-emits a yellow-green light; this can reach the silver halide, e.g., AgBr, and blacken the plate. The layer of fluorescing molecules, however, must be quite thin otherwise absorption will occur and defeat the purpose.

* See Hirschlaff's book *Fluorescence and Phosphorescence*, p. 67-69, Chemical Publishing Company, Brooklyn, New York (1939).

Biochemical Aspects: Uranium Poisoning

Radioactive elements may be precisely determined in amounts smaller than those possible with most other elements. Uranium is a radioactive element. From this property alone studies on the action of uranium on living organisms should be particularly enhanced. Consider that few other non-radioactive elements can be detected in amounts as small as 10^{-12} gram as is the case with uranium by use of a sensitive Geiger-Mueller Counter.

Consider also that counter tubes can be constructed for placement in organs and in remote regions of living organisms. In this way the distribution of uranium in all its quantitative phases might be studied during the actual metabolic processes of an organism. This is unlike practically every other mode for study of toxic substances in that the dead tissue must be subjected to a series of altering reactions before a reaction is obtained which characterizes the presence of the element for which the search is being conducted. Uranium is approximately as toxic as arsenic, one gram of uranium giving off 24,770 alpha particles every second (Kovarik and Adams, 1932). By use of certain types of Geiger-Mueller Counters less than one alpha particle passing through a gaseous chamber per hour may be detected.

The subcutaneous injection of from 0.5 to 2.0 mg. of UO_3 for every kilo of bodyweight of cats, dogs, or rabbits, will cause death. Ingestion of soluble uranium salts produces intense gastrointestinal irritation with corrosion of the mucous membranes; and ultimately resulting in gastroenteritis. Inhibition of the action of digestive ferments occurs after ingestion of small amounts of uranium salts. After oral administration of this poison rapid action is not noted, even in fatal doses the symptoms are delayed for some time. The symptoms of uranium poisoning begin with muscular weak-

ness, attenuation of digestive action, and hyperpyresis.

Acute nephritis is characteristic of uranium poisoning. The introduction of small amounts of uranium into the system over long periods of time will cause chronic nephritis, their ultimate result being the same, however. Like mercury, phosphorus, and arsenic, destruction of the renal tissues occurs with eventual hemorrhage of the substance of the kidney. Glycosuria occurs and this is due to the lowered glucose threshold of the kidney. During uranium poisoning the carbohydrate metabolism remains about normal.

Uranium nephrosis is of particular clinical interest. Uranium nephrosis has been studied by cross perfusion experiments and it has been found that administration of uranium in large doses to dogs produces an early glycosuria which is concomitant with an increase in loss of water and chlorides. Polyuria is first produced in uranium poisoning this being followed by oliguria and finally cessation of micturition-anuria.

A rise in urinary phosphorus occurs and this is due to a lowering of the phosphorus threshold. The cells of the renal tubes are destroyed this leading to a decrease in chlorides which return to normalcy by the end of the second day. Lesions are formed in the first segment of urinary tubes with edema of the apical cytoplasm.

When uranium is injected it causes a local reaction. The intense local irritation that is produced causes excitement in rats which have been injected with 5 mg. for every kilo of bodyweight. The absence of chlorides causes a rise in blood chlorides, this reaching a maximum in 24 hours. Uranium causes an increase in all the blood lipoids. Also, a decrease in nonprotein nitrogen and blood sugar occurs. In studies by H. Larson in 1936 it was found that the xylose tolerance in rabbits decreased after injection of 0.2 to 1.0 mg. of uranium for every kilo of bodyweight and after repeated in-

jections the rabbits apparently developed a resistance to uranium since the xylose tolerance tends to return to normal. It was found in these studies that the xylose tolerance is not a reliable indication of kidney function.

An interesting concept of uranium poisoning is in the following experimental work. An artificial tissue was prepared by impregnating an agar gel with sodium nucleate. Through this "tissue" a solution of uranyl nitrate was allowed to diffuse. The result of the reaction between the sodium nucleate in the gel and the uranyl salt was in the formation of an opaque white precipitate of uranyl nucleate. An action occurs along similar lines in the actual living gel (tissue)—the uranyl salt reacting with the proteins to form salts with a simultaneous destructive and corrosive action. A gel may be prepared by use of sodium nucleate singularly and this may be used with similar results when treated with uranyl salts.

Related to this is the salt prepared by K. Hagenguth in 1936. This investigator succeeded in preparing the uranyl salt of cytosylic acid. The material used initially was sodium nucleate. A reaction product from uranyl salts and tissues has been described—this being uranyl albuminate. The substance is in the same category as the other protein derivatives of the uranyl group.

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6

SPECIFIC METHODS IN URANOMETRY

Introduction

URANOMETRY refers to the methods used in the detection and determination of uranium. Like other forms of analytical chemistry, uranometry should include precision incorporated with practicability. The two extremes in uranometry are illustrated, one, by the intricate techniques used by the researcher which involve equipment such as the mass-spectrograph. The other is illustrated by the prospector hand-examining a specimen believed to be uranium-radium bearing, judgment being based on simple properties like color, specific gravity, hardness, luster and feel.

The methods to be presented are of a widely varying nature. They are adapted to a still wider range of problems. In uranometry, as in many other forms of chemical analysis, the test is a function of the material to which it is applied with special reference to the environment and the human hand which directs the manipulations. As is apparent in many cases tests are independent of the human equation. In some instances, however, the precision of the determination is a function of the magnitude of the human error which is often-times invariably present. A fundamental consideration in this presentation is to reduce procedures to the greatest amount of objectivity. This is shown by the particular reference to colorimetry, electrolytic methods, titrimetry and others which were heretofore governed entirely by the skill and patience of the analyst. In the latter modes of testing instrumental means are emphasized, accurate analysis gener-

ally implying that instrumental methods have been used or were preferred. The great chemist Feigl has used a statement which clarifies our position considerably as regards the chemical analysis for uranium. Feigl has remarked that a reaction that is perfectly reliable for the detection or determination of a particular material in a certain environment may fail completely if it is applied under other circumstances. Consequently the choice of suitable methods must be made in the light of the possible variations. Since chemical analysis generally rests on the possibility of converting the substance to be detected or determined into another characteristic form or combination the choice of method must be intelligent. It is obvious that the demands on chemical reactions with respect to their analytical applicability are quite different when the problem at hand is qualitative rather than quantitative.

Aside from the procedures in uranometry which involve chemical reactions are the spectroscopic methods, i.e., by use of the visible light spectroscope, the X-ray spectrograph, and the mass-spectrograph. While these are restricted in that extensive practical application is not ordinarily possible certain advantages are found in their use. Other than the ordinary spectroscope and the mass-spectrograph, the X-ray spectrograph stands out as being a most reliable instrument for absolute confirmation of the type and structure of components in a mixture. The gravity of its evidence far outweighs most other methods not in its immediate category. The X-ray spectrograph is an instrument of precision and delicacy but for effective and adequate results its use should be confined to the hands of an expert who is not only well versed in methods of use but also versed in methods of interpretation of spectrograms.

There are forms of analysis given here which are now obsolete. The present value of these is two-fold. From a historical standpoint they may be interesting, but of more

importance is the chance that they may contain that new aspect, or approach which may lead to a superior form of uranium analysis. There are some present day uranium analyses which are becoming obsolete, and these are important for the same reasons.

But the forms of analysis which have given way because of their impracticability or limitations in accuracy now give way to new forms of analysis prominent because of their objectivity and reliability. Polarographic methods, fluorescence analysis, spot tests, and others are of an engaging nature not only because of their value as analytical methods, but also because of their importance in revealing new facts about the chemistry of uranium itself. A new method of chemical analysis always reveals new secrets about the material upon which it is being used. With the wider use of different methods of analysis and tests more information will be revealed concerning the nature of uranium.

Mother nature is still the greatest chemist. Man has yet to devise methods of detection which will surpass those in delicacy found in nature. The pleochroic halos formed by extremely minute amounts of radium exceed, by about a hundred thousand times, the best existing electrical means for the detection of this element. It would seem from this that man's biased admiration of his own analytical ability is rather unfounded.

Solution of the Specimen

Obviously discussion of methods for solution of uraniferous ores depends on the chemical nature of the specimen as well as the solvent. For an effective practical and theoretical approach to solution of specimens the reader is referred to the previous chapter on the chemistry of uranium. Generally, most ores respond to treatment with concentrated acids

and a few secondary uranium minerals are soluble in water. The addition of alkalis to solutions which contain uranium generally precipitate the greater part of the element in the form of the uranate.

Uraninite, which consists mainly of UO_2 , is soluble in aqua regia and nitric acid. Other acids dissolve uraninite with difficulty although heating aids solution. Uranium may be extracted from pitchblende, U_3O_8 , by use of similar reagents. It will be noted, however, that after extraction of uranium from a mineral the residue often contains traces of foreign elements and silicates which carry down a small amount of uranium. These interfere with the accuracy of the uranometry. Should the residue be suspected of containing additional traces of uranium the procedure for removal of the traces is to treat with hydrofluoric acid. After this acid treatment the residue is dried and then fused with sodium carbonate and re-extracted with hydrochloric acid.

For extraction of uranium from its ore more drastic technique may be required. Some specimens of pitchblende may be suitably extracted by heating one part of the ore with six parts of concentrated sulfuric acid in a closed tube for several hours at 175°C . The residue from this is dissolved in a solvent which may be an acid solution. Solution from this yields uranous and uranyl sulfates. This treatment was used by Hillebrand in 1891.

Fusion is a form of metathesis which may be required. Probably the most used procedure is mixing with anhydrous sodium carbonate or other agent of a like nature and heating for prolonged periods at high temperature.

Characteristic Reactions

A number of characteristic reactions provide bases for detection and estimation of uranium. These have been dis-

cussed under The Chemistry of Uranium, although it is advantageous to direct attention to those reactions on which more commonly used tests and procedures depend. For example, in 1912 Treadwell and Hall enumerated a number of such reactions. Probably the most important is the precipitation of bright yellow uranates when alkalis, e.g., ammonium hydroxide, are added to solutions which contain soluble uranium salts. In the uranate precipitation an intermediate stage occurs in which uranyl hydroxide is first formed with the uranate then being formed according to the following reaction :



where R is practically any highly dissociated hydroxide, preferably being NH_4 , K, or Na.

Many other reactions of this type are known which are of varying value for uranium analysis. Barium carbonate is an especially effective reagent since it completely precipitates uranium from solutions in the cold, a double salt, barium uranyl carbonate being formed in the reaction. The sulfide ion coadunates with the uranyl ion to form dark-brown uranyl sulfide, a substance which is soluble in dilute acids and also in ammonium carbonate solution. It follows that in acid solutions hydrogen sulfide causes no precipitation, a reagent such as ammonium sulfide being necessary.

Uranyl ferrocyanide is a compound of import. The brown uranyl salt is produced when soluble ferrocyanides, e.g., the potassium salt, are added to solutions containing uranyl ions. Copper forms a similar brown precipitate with ferrocyanides but the two may be differentiated by addition of potassium hydroxide solution, this resulting in a yellow coloration from the formation of the uranate. The solubility of uranyl ferrocyanide, as differentiated from the solubility of the copper salt, is another factor which discriminates them. In actual

test the solution to be examined is acidified with hydrochloric acid and a small amount of sodium chloride is added to prevent colloidal precipitation.

Separation of Interfering Elements

The analysis for uranium is interfered with when alkali and alkaline earth elements are present. To separate these one of several methods may be used. If a solution of uranium and alkali and alkaline earths is precipitated by ammonium hydroxide a portion of the alkali and alkaline earths is carried down by the ammonium uranate. This prevents complete separation. Hillebrand (1900) separated these elements by several precipitations with ammonium hydroxide. In 1904 Kern verified this method in addition to finding that complete separation is effected after three precipitations.

G. Alibegoff (1886) separated all of these, except barium, with the precipitation being made by adding a slight excess of fresh emulsion of mercuric oxide to the boiling solution which contains ammonium chloride or ammonium nitrate. The solution is boiled for a few minutes and then cooled in cold water. The precipitate is washed by decantation with cold dilute ammonium chloride and placed in a platinum crucible, with the filter paper, and cautiously heated (at first), finally being ignited over a blast lamp. The residue consists of pure urano-uranic oxide. Calcium and strontium cause little trouble, otherwise the separation is satisfactory. Interference of this kind may be overcome by boiling several times, during washing by decantation, with a solution of ammonium chloride and each time rapidly cooling the solution before pouring off the supernatant liquid. The calcium and strontium are determined by the usual methods after removal of the mercury by hydrogen sulfide.

COMPOSITIONAL FREQUENCY OF URANIUM MINERALS

(An Approach to Uranium Assay)

<i>Most Frequent</i>	<i>Less Frequent</i>	<i>Rarely or Never</i>
Oxides	Carbonates	Iodides
Vanadate	Phosphates	Bromides
	Sulfates	Fluorides
	Silicates	Sulfides
	Aqua salts of these.	Acetates
		Nitrates

For approximately five or six uranium compounds which have been prepared in the laboratory one compound of uranium occurs in nature.

Gravimetric methods are not entirely satisfactory for the separation of uranium from the alkali and the alkaline earth metals. By electrolyzing an acetate solution of these elements a perfect separation can be obtained according to Kern (1904). Uranium can be readily separated from sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, and barium by electrolytic methods. The technique was used in 1879 by E. F. Smith for separating uranium from alkali and alkaline earths, and the *rare earths*, in the analysis of rare minerals. A peculiar property of uranium is that it is not deposited as a metal on the cathode, but as a hydrated oxide. Molybdenum is the only other metal known which, like uranium is deposited as an oxide on the cathode. Kern used this method with favor because of its simplicity and the short time required for determinations.

Foullon separated uranium from calcium by ammonium sulfide although the separation was incomplete. Precipitation in the presence of ammonium chloride provided a more complete separation. The separation of barium, calcium, and strontium from uranium was proposed by Fremy. This was

used by Rammelsberg, *et al.* Foullon separated calcium as the oxalate in an excess of ammonium carbonate. This method was used by Kern and others. Separation is accomplished by heating alkali uranates and ammonium chloride in hydrogen. The chloride of the alkali is extracted by water while the alkaline earths are precipitated by sulfuric acid and alcohol (Rammelsberg, 1885).

The separation of uranium from members of the fifth and sixth groups may be accomplished by hydrogen sulfide. This method depends on the pH of the solution and its temperature. Separation is best obtained when 1 cc. of nitric acid (1:2) is present for each 50 cc. of test solution. The solution is then saturated with gas while cold. The addition of hydrochloric acid in amounts of 1 cc. for each 50 cc. also produces good results. When the acid exceeds 2.5 cc. per 50 cc. incomplete precipitation of lead results, this interfering with the accuracy of the uranium analysis. Less acid must be used if the precipitation is performed with hot solutions. Precipitation from hot solutions is not recommended.

Kern found that 5 cc. of concentrated acid in 250 cc. of solution produced perfect separation of uranium from metals of the fifth group, whose sulfides are most insoluble, i.e., lead and cadmium, and also from copper. These conditions appear to be suitable for other members of this group. Lead requires the least amount of free acid to retain it in solution whereas the others follow in order of succession: cadmium, mercury, bismuth, copper, and silver.

The methods for separation of members of the fifth and sixth groups ordinarily depend on the solubility of uranium hydroxide and sulfide in an excess of a strong solution of an alkali carbonate. The hydroxide and sulfides of the other members of these two groups are, with the exception of iron and nickel, insoluble in alkali carbonate solutions. The hydroxides of these two metals are only slightly soluble in

strong alkali carbonate solution; in cold dilute solutions they are practically insoluble.

Probably the most difficult element to separate from uranium is iron. A great number of methods have been proposed but the best known is Pisani's Ammonium Carbonate Method or perhaps Patera's Sodium Carbonate Method. Neither of these is entirely satisfactory. Rose used ammonium carbonate, followed by ammonium sulfide (1862). In this method the iron is precipitated, however, the procedure is not satisfactory when dealing with small amounts of specimen. Rheineck's basic acetate method is more satisfactory, functioning more accurately for large amounts of uranium in solution.

The interference of phosphoric acid in uranometry has been mentioned but it should be emphasized more strongly. Before accurate analysis may be made for uranium complete separation from any phosphoric acid present is essential. In Reynoso's method (1852) the uranium is placed in solution as a nitrate with a small amount of nitric acid. The solution is then diluted to 150 cc. and a strip of tin is added and boiled. The phosphoric acid unites with the tin forming insoluble tin oxyphosphate. This insoluble precipitate is filtered off and washed. The filtrate is alkalinized with ammonium hydroxide while the precipitate is treated with acetic acid. If the precipitate does not dissolve entirely more nitric acid is added and the precipitation by tin repeated. The solution is then heated to 100° C. and refiltered. The precipitate is washed with warm water, after this treatment rarely containing any uranium. Tin in the filtrate is removed by hydrogen sulfide and the filtrate from the tin sulfide is boiled until all the hydrogen sulfide is expelled. The uranium is then determined by the usual methods. According to W. Hintz (1869) separation is complete by this method.

In 1856 Knopp and Arendt devised a method whereby

phosphoric acid could be separated from uranium. They fused the ignited mass of uranium and phosphoric acid with potassium cyanide and potassium carbonate. From this the phosphoric acid was dissolved out by warm water as a soluble alkaline phosphate. The uranium remains as the oxide and after reignition is weighed or is dissolved in acid and precipitated by ammonium hydroxide. The phosphoric acid filtrate is precipitated by magnesia mixture and weighed as magnesium pyrophosphate. In the separation sodium carbonate may be substituted for the potassium carbonate.

Reichardt's method is based on the direct precipitation of phosphoric acid from the acetate as uranyl ammonium phosphate, provided the uranium is in excess. The precipitate is filtered and washed and dissolved in sodium carbonate solution. This is added to a solution of magnesia mixture, causing the precipitation of phosphoric acid as magnesium ammonium phosphate. If iron is present it is first precipitated from a nitric acid solution and boiled. The phosphoric acid in the filtrate is precipitated as magnesium ammonium phosphate and the uranium is then determined by the usual methods after expelling the carbon dioxide.

Fresenius and Hintz have a method for separation of uranium from phosphoric acid. In this method other elements respond as well. Arsenic may be separated from phosphoric acid and both of these from copper, while uranium and iron may also be separated. The solution is slightly acidified by hydrochloric acid and an excess of potassium ferrocyanide is added, this being saturated with sodium chloride (cf. data in the previous chapter). The ferrocyanides of copper, uranium, and iron, are washed by decantation and are subsequently decomposed by a warm solution of potassium hydroxide. The solution is filtered and washed with dilute ammonium chloride solution until no ferrocyanide appears in the washings. The mixed hydroxides are added

to dilute hydrochloric acid and any residue which remains is again treated as before. The hydrochloric acid solution is free from arsenic and phosphoric acid. The copper, iron, and uranium ferrocyanides may then be separated by the usual methods.

Friedel and Cumenge (1900) separated phosphoric acid from uranium by dissolving the specimen in nitric acid and precipitating the phosphoric acid with ammonium molybdate. Leppierre and Corvalho (1913) separated phosphorus from uranium when the acidity of the solution was nearly neutralized by sodium hydroxide and sodium carbonate was added. In the presence of an excess of iron the solution was boiled to precipitate the iron as ferric phosphate. The remaining iron was carried down as the basic acetate.

The separation of vanadium from uranium has been discussed by Kern (1904). Low separated vanadium and uranium by ammonium acetate, sodium monohydrogen phosphate, and acetic acid in investigations performed in 1914. This mixture was boiled and the vanadium was precipitated completely after two operations. Hillebrand (1891) separated vanadium and uranium by treating with nitric acid in a porcelain boat, evaporating to dryness, and passing hydrogen chloride over the heated tube containing the boat. The vanadium passes off as the oxychloride leaving the uranium. Hillebrand also separated the two by evaporating a nitric acid solution to dryness and extracting with cold water. The vanadium is removed by a second evaporation with nitric acid. The uranium in the precipitate is removed by a second treatment of the residue. Konig (1913) separated vanadium and uranium by treating the solution with ammonium carbonate and ammonium hydrosulfide. This is followed by hot acetic acid. Auger (1920) found cupferron did not precipitate uranyl salts but that in acid solution the reagent was reduced by zirconium. The resulting uranium salt was then

precipitated by cupferron (cf. section on organic precipitants in this chapter). The cupferron precipitate is insoluble in chloroform and this may be used to separate uranium and vanadium.

A. C. Langmuir (1904) used a distinctive method for the separation of vanadium from uranium in carnotite. The finely powdered carnotite is dissolved in the smallest possible amount of nitric acid. A residue which remains consists mainly of silica, this being filtered off. The filtrate is diluted to 500 cc. with water and precipitated by mercurous nitrate. The precipitation is performed by adding a concentrated solution of mercurous nitrate to the nitric acid solution of the ore which was previously nearly neutralized by yellow mercuric oxide. The vanadium precipitates on addition of the mercurous nitrate. The solution is then boiled and filtered. Other elements such as chromium, molybdenum, and tungsten are precipitated as mercurous salts. The precipitate is washed with a warm dilute solution of mercurous nitrate and dried. After ignition it is weighed as V_2O_5 . Any excess of mercury present in the filtrate is removed by hydrogen sulfide. After expelling the hydrogen sulfide by slow boiling the uranium is determined by the usual methods.

Pierle separated uranium from vanadium by evaporating a solution of the ore to dryness with an excess of nitric acid. The residue is moistened with nitric acid and extracted by ether. The ether will dissolve the uranium alone and the vanadium salts will remain intact in the other fraction. The uranium residue which contains vanadium may also be extracted by use of glacial acetic acid instead of ether, the reagent used consisting of 5% nitric acid in glacial acetic acid. The vanadium is not attacked under these conditions.

The separation of vanadium from uranium is not too difficult unless phosphoric acid is present, in which case the separation becomes troublesome. Friedel and Cumenge

(1900) separated vanadium from uranium by evaporation to dryness with nitric acid. The uranium is then extracted from the dry mass with a warm dilute solution of ammonium nitrate. For this separation no phosphoric acid should be present since it makes the uranium oxide with which it is combined, insoluble in dilute ammonium nitrate solution.

Blair (1913) determined uranium in the presence of vanadium as $V_2O_5 \cdot 2UO_3(NH_4)_2O \cdot H_2O$. Ammonium acetate, prepared by adding 30 per cent acetic acid to concentrated ammonium hydroxide until the solution is acid to litmus, is added to slightly acidify the uranium solution containing the excess of vanadium. Ammonium uranyl vanadate is filtered off, ignited at a low red heat, and weighed as $V_2O_5 \cdot 2UO_3$.

A method especially for carnotite is that of O. P. Fritchie. In this method the mineral is powdered finely and decomposed at $100^\circ C$. by 10 cc. of nitric acid and taken up with an equal amount of water. The solution is then neutralized with a saturated solution of sodium carbonate, this being added 5 cc. in excess together with 20 cc. of 20% sodium hydroxide solution. This is then boiled for one half hour and the precipitate allowed to settle. The vanadium, uranium, and iron are precipitated by sodium carbonate but when a moderate excess is added with the sodium hydroxide solution, the vanadium is dissolved and the uranium and iron remain insoluble.

Uranium is easily precipitated by sodium carbonate and sodium hydroxide in the presence of iron salts. The precipitate is washed with sodium hydroxide and the uranium and iron separated by the ordinary methods and each determined volumetrically by titration with standard potassium permanganate solution. Prior to the volumetric determination, however, their sulfates are reduced at $100^\circ C$. with aluminum. Fritchie's method dates back to 1900 and earlier.

The separation of uranium from cobalt, nickel, and zinc

may be accomplished in a variety of ways. Walcott Gibbs (1865) separated uranium from these elements by hydrogen sulfide. The solution was added to sodium acetate and boiled, hydrogen sulfide gas then being passed through the boiling solution for a half an hour. The interfering elements are precipitated as sulfide while uranium and manganese are not. The precipitate is washed with cold hydrogen sulfide water and the uranium determined in the usual manner.

Rose (1862) used sodium carbonate for his separations. The precipitation of uranium is complete from uranic solutions which contain a small amount of free acid. Hydrochloric acid and barium carbonate in excess are allowed to diffuse through the water and then allowed to stand for 24 hours. The presence of ammonium chloride is necessary to keep the cobalt, nickel, and zinc, in solution. Uranium is separated from the excess barium carbonate by dissolving the precipitate in hydrochloric acid and adding dilute sulfuric acid. The uranium in the filtrate is precipitated by ammonium hydroxide and determined as the oxide.

Two rather troublesome methods for separation mentioned previously are those of Patera and Pisani. Kern stated that separation is complete in an excess of sodium carbonate provided the solution is boiled for 15 minutes before filtration. No uranium remains with the iron and this is precipitated and may be filtered and washed.

Konig (1913) removed iron, nickel, and cobalt from uranium by the electrolysis in ammonium oxalate solution, the electrolysis being continued until the oxalate is entirely converted into the carbonate. Buckminster and Smith also separated mercury, cobalt, and nickel from uranium by electrolysis.

Rheineck (1871) separated iron and uranium by nearly neutralizing the nitric acid solution with sodium carbonate and adding sodium acetate. This is diluted and boiled, the

iron being precipitated. The iron precipitate will carry uranium unless heating is carried on in an excess of water.

Brearly (1903) boiled phosphates, uranium, and aluminum in an excess of sodium carbonate with ammonium chloride and filtered after two hours of this treatment. Walker (1898) precipitated iron by sodium hydroxide in an excess of hydrogen peroxide. The precipitation occurs best in a hot solution and the filtrate contains all of the uranium.

Ditte (1877) heated the oxides of iron and uranium in hydrogen and then in hydrogen chloride at red heat. The iron passes off as the chloride. Burkner (1878) used a method whereby the oxides of uranium and iron are reduced by a current of hydrogen and the iron is dissolved by dilute hydrochloric acid, leaving the uranium. Zimmermann (1879) boiled the solution in an excess of ammonium thiocyanate together with sodium bicarbonate, the latter being added until the red color disappears. The iron precipitate is free from uranium. Becker and Jannasch (1915) separated iron from uranium by hydroxyquinoline. Kern used Langmuir's method. Rammelsberg (1885) separated uranium from manganese, zinc, nickel, and cobalt by adding pure barium carbonate to a slightly acid solution together with ammonium chloride (cf. Rose's Method).

Pierle (1920) separated uranium from molybdenum and tungsten by extraction with ether. Hillebrand (1891) precipitated the rare earths from a slightly acid solution with oxalic acid at 60° C. The oxalates were removed from the uranium by evaporation and ignition.

The ether separation of Langmuir has been discussed at length by Kern. The latter investigator modified the method in that separation depends on the extraction of ferric chloride, in aqueous hydrochloric acid, by alcohol-free ether with the retention of uranyl chloride in the aqueous fraction. The uranyl chloride is insoluble in ether provided the latter is free

from alcohol. The most complete separation of iron from uranium is by ether with hydrochloric acid of specific gravity 1.10.

Beryllium, chromium, and zirconium may be separated from uranium by warming with hydrogen peroxide and reprecipitating when large amounts of beryllium are present (Wunder and Wenger, 1914). Gibbs (1873) separated chromium by sodium hydroxide and bromine. On boiling the chromium was oxidized. The sodium uranate was filtered off. Ditte (1877) heated oxides of uranium and chromium in hydrogen and dissolved the uranium in nitric acid, leaving the chromium.

This method has been found somewhat unsatisfactory by others. Classen (1885) separated chromium by electrolysis of an oxalate solution. Walker (1898) separated zirconium and uranium by fusion with sodium thiosulfate and extracted by cold water. Hydrogen peroxide and sodium hydroxide were added and zirconium was precipitated by heating. The uranium remained in solution. Angelotti (1921) separated zirconium and uranium by cupferron. The zirconium precipitated in sulfuric acid solution while the uranium remained in solution.

Gravimetry

Gravimetric determination of uranium is often discarded in favor of other methods which are easier to use and which are more economical. But with the greater availability of more sensitive balances which obviously aid in reduction of a part of the error gravimetry assumes extended importance in uranium analysis. This is particularly patent in the case of the microbalance. In this weighing is extended with little difficulty from three to six places beyond values formerly obtained by use of old equipment.

Analytical air-damped balances for ultra-rapid weighings are available and which make possible sixty different weighings per hour. Air-damped balances with mechanical manipulation of all weights are features which re-enforce the value of gravimetry in the uranium assay. But of more interest are the microbalances. Industrial microbalances may be obtained which have a sensitivity of one gamma (one-thousandth milligram, i.e., one microgram) and which have a number of special features to aid in rapidity and ease of operation. For example, some microbalances are equipped with automatic damping devices, optical reading accessories, and elimination of fractional weights through chains or other such arrangement.

A rapid and accurate method for the determination of uranium was described in 1919 by Scholl. The procedure is known as Scholl's Rapid Method. In it the uranium is extracted from its ore with a dilute nitric acid solution (1:1), diluted, and filtered. Ferric chloride and sodium carbonate are then added to precipitate the vanadium and iron and a greater part of the aluminum. The uranium is precipitated from the filtrate by boiling with sodium hydroxide and purified by dissolving in nitric acid. It is then precipitated by ammonium hydroxide as ammonium uranate, this being ignited to U_3O_8 and weighed.

Procedure. To a sample of the ore containing about 0.2 gm. of uranium oxide, add 25 to 50 cc. of 1:1 nitric acid and heat until all the uranium is in solution. Keep warm several hours if necessary to insure solution. Dilute with warm water to about 250 cc. and filter. Add ferric chloride equivalent to about three times the weight of the vanadium present. Add slowly to the cold or slightly warm solution solid sodium carbonate until all the acid is neutralized, with about 1 gm. in excess, keeping the beaker covered with a watch glass. Place on a hot plate and heat to about 90° C. but do not boil.

Keep warm for at least 15 min. Filter. The precipitate contains all the iron and vanadium and the greater part of the aluminum. Neutralize the filtrate slowly with nitric acid until the uranium begins to precipitate and boil to eliminate most of the carbon dioxide. Add sodium hydroxide in excess and boil for 15 min. Filter. The filtrate contains the remainder of the aluminum and any vanadium not previously precipitated. Dissolve the precipitate in dilute nitric acid and heat to about 90° C. Add an excess of ammonium hydroxide and boil. Filter and ignite the precipitate and weigh as U_3O_8 .

In case of doubt as to the purity treat the precipitate with dilute warm nitric acid. Filter and ignite, and weigh the insoluble matter. Subtract this from the previous weight and report the result as U_3O_8 . Some iron is usually found in the precipitate, this being carried in the reagents as an impurity. The final precipitate of uranium is generally vanadium-free but it is well to test the U_3O_8 for this element by dissolving in nitric acid and adding hydrochloric acid, followed by hydrogen peroxide. The addition of hydrochloric acid increases the delicacy of the test.

GRAVIMETRIC FACTORS AND THEIR LOGARITHMS FOR URANIUM

*Modified after N. Lange and based
on Atomic Weight 238.07*

<i>Log. of Factor</i>	<i>Factor</i>	<i>Entity</i>	<i>Factor</i>	<i>Log. of Factor</i>
—10				—10
10.0548	...1.134...	$\text{UO}_2 \rightleftharpoons \text{U}$	0.8815	...9.9452
10.0716	...1.179...	$\text{U}_3\text{O}_8 \rightleftharpoons \text{U}$	0.8480	...9.9284
10.0168	...1.039...	$\text{U}_3\text{O}_8 \rightleftharpoons \text{UO}_2$	0.9620	...9.9832
9.7474	...0.559...	$\text{U}_3\text{O}_8 \rightleftharpoons \text{UO}_2(\text{NO}_3)_2^*$	1.17875	...10.2526

* = $6\text{H}_2\text{O}$

Patera's assay was found by Kern to be uniform in results for pitchblende. In Patera's assay one to five grams of the powdered mineral are dissolved in hot nitric acid which has been diluted 1:2 with water. This is then diluted and ferric chloride added if necessary, being followed by sodium carbonate solution in excess. The mixture is boiled and the precipitate is filtered off and washed with hot water. The filtrate contains all of the uranium and only a small trace of other metals. The solution is then neutralized with hydrochloric acid and the carbon dioxide expelled by boiling. Orange-yellow sodium uranate is precipitated by sodium hydroxide, the precipitate being filtered off and washed with hot water and dried. The filter paper is ignited in a platinum crucible and the dried uranate is added and the contents of the crucible ignited strongly. After cooling the material is placed on a small piece of filter paper. The free alkali in the uranate is washed out with hot water and the filter paper and contents, are dried and reignited. The pure sodium uranate is weighed and the $\text{Na}_2\text{U}_2\text{O}_7$ is equivalent to 88.5 parts of U_3O_8 .

According to C. Winkler the presence of excessive amounts of copper increases the value in Patera's assay. A small amount of unprecipitated copper is carried over with the alkaline solution.

Another gravimetric method for the determination of uranium is that of Fresenius and Hintz (1895). The ore is digested in acid and then evaporated to dryness. The silica present is dehydrated and the uranium extracted with dilute hydrochloric acid. Potassium ferrocyanide is added and the solution is saturated with sodium chloride. After the precipitate has settled, it is filtered and washed with sodium chloride solution and then decomposed by potassium hydroxide. The precipitate in which the uranium is present as potassium uranate is then washed from the ferrocyanide with

a solution of ammonium chloride and ammonium hydroxide. The residue, free from phosphorous and arsenic, is dissolved in hydrochloric acid and nearly neutralized by ammonium carbonate which is added in excess. The iron and aluminum are filtered off and the filtrate is acidified and heated. Hydrogen sulfide is added, together with ammonium hydroxide to precipitate the uranium, this being then ignited to urano-uranic oxide or further reduced to the lower oxide by hydrogen.

Accurate analysis for uranium was accomplished by the method of W. W. Scott (1932). The residue obtained from the evaporation of the nitric acid solution of the ore is treated with a reagent consisting of acetic acid and nitric acid. The uranyl ions and a small amount of vanadium enter into solution. The uranyl salt is precipitated by ammonium hydroxide and weighed as urano-uranic oxide. An accuracy of 0.5% is claimed for this method. Borntrager's method (1898) consists of digestion of the ore with nitric acid, diluting and filtering. An excess of sodium carbonate is then added and the uranium, together with traces of other metals are dissolved when the solution is boiled and filtered. Sodium hydroxide is added to the filtrate to precipitate the uranium as sodium uranate, the precipitate then being dissolved in hydrochloric acid. The uranium is reprecipitated by ammonium hydroxide and, after washing, is ignited to the oxide.

One of the simpler methods for the estimation of uranium, especially when in comparatively pure solutions is precipitation as the uranate by ammonium hydroxide, isolation and ignition of this precipitate, the results being interpreted in terms of U_3O_8 . This procedure has been followed rather extensively and was described at length in 1904 by Kern.

The determination of uranium as the oxide was first accomplished in 1840 by Peligot. Uranyl salts were mixed

with ammonium hydroxide, the result of the reaction being the uranate. The uranate is insoluble in alkali carbonate solutions and is slightly soluble in water. In water which contains ammonium hydroxide, ammonium nitrate or chloride, it is insoluble. The presence of tartaric acid, oxalic acid, or non-volatile organic substances prevents precipitation of ammonium uranate. If the solution contains alkalis or alkaline earths a portion of these will be carried along with the uranium.

Berthier's method is another early procedure being used in 1840. In this analysis a complete separation is obtained provided the solution has been previously nearly neutralized by ammonium hydroxide and no carbonates are present. The precipitate is usually black, obtained from the addition of ammonium sulfide, although it may be red-brown. An excess of precipitant forms a brown color. This is due to soluble uranyl sulfide formed when the ammonium sulfide used contains ammonium thiosulfate or other such salt as an impurity. The precipitate is dark when no thiosulfate is present. The thiosulfate is produced by the oxidation of the sulfide in the presence of oxygen. By this method a complete separation of uranium from the alkali and alkaline earths is obtained.

The yellow-green mass of ammonium uranate formed on precipitating uranium with ammonium hydroxide in the presence of an ammonium salt is converted into a darker crystalline form by boiling for twenty minutes and allowing to settle at room temperature.

The complete oxidation of uranium to urano-uranic oxide is accomplished by igniting the ammonium uranate in either a platinum or a porcelain crucible over a blast lamp. This is done by having the crucible in a slanting position and igniting intensely over the lamp for about ten minutes, after

which the crucible is allowed to cool in a slowly decreasing bunsen flame.

Fairly (1890) used hydrogen peroxide as a precipitant in excess for uranium. However, an excess of sodium, potassium, barium, calcium, hydrochloric acid, nitric acid, sulfuric acid, prevent complete precipitation.

In 1906 Mazzucchelli used the same method forming the tetraoxide of uranium as the precipitate, provided ammonium chloride was added in molar quantities and the temperature did not exceed 70°C . Also, provided the hydrogen peroxide was present in excess. A solution of 0.01 N. ammonium chloride is used as the wash water. An excess of other salts prevents complete precipitation.

Uranium may be determined as the phosphate. However, the precipitation of uranium as the alkaline phosphate is not entirely satisfactory since the precipitate is gelatinous, and therefore difficult to handle as well as difficult to wash free from the alkali. This difficulty has been overcome by adopting the method to volumetric means which is the reverse of the volumetric estimation of phosphoric acid by standard uranium solution. The uranium in solution as the acetate is titrated by a standard sodium hydrogen ammonium phosphate solution (NaH_2PO_4). This is added until a drop of the precipitated solution, when brought into contact with a drop of fresh potassium ferrocyanide solution, does not produce a brown coloration.

The quantitative determination of uranium by alkali phosphate was first suggested by Leconte in 1853 and was later investigated by Pisani in 1862. But owing to the difficulties encountered in filtering and washing the voluminous precipitate, a greenish-yellow slimy mass, the method did not come into prominent use.

The estimation of uranium as phosphate may be accom-

plished when the precipitant used is ammonium phosphate in the presence of ammonium acetate. The precipitate of $(\text{UO}_2\text{NH}_4\text{PO}_4)$, on boiling, forms a crystalline mass which is easily filtered and washed. The ignited precipitate, previous to weighing, is moistened with concentrated nitric acid, dried, and reignited at temperatures equivalent to a low red-heat in a porcelain crucible. If the temperature is increased, and especially if the ignition is performed strongly in platinum crucibles, the material is reduced to the pyrophosphate, $(\text{UO}_2)_2\text{P}_2\text{O}_7$. Whenever this occurs reoxidation may be performed by moistening the green mass with concentrated nitric acid and reigniting at low redness. The ignition should be conducted in porcelain vessels.

Brearly (1903) used microcosmic salt and sodium thiosulfate to precipitate uranium. The precipitate obtained in this manner is not difficult to filter and wash but is hygroscopic and must be ignited and weighed immediately after its separation. Noyes, et al, in 1908, precipitated uranium as the phosphate in the presence of ammonium salts to encourage the formation of the double salt, uranyl ammonium phosphate, which ran through the filter.

Bureau of Mines Method

The United States Bureau of Mines has used a satisfactory method for the gravimetric determination of uranium in carnotite. Their official procedure was adopted from technique used in the laboratories of Ledoux and Company in about 1915. The method of the Bureau of Mines was discussed by C. W. Davis in 1923 and although tedious is quite accurate.

Résumé. The ore is treated with hydrochloric acid and nitric acid and, after evaporating to dryness, is extracted with dilute hydrochloric acid, filtered, and washed. If the

ore is not completely decomposed the residue is ignited, treated with hydrofluoric acid and evaporated to dryness twice with hydrochloric acid to expel all of the hydrogen fluoride.

The residue is extracted with dilute hydrochloric acid and the filtrates and washings are saturated with hydrogen sulfide, filtered, and boiled to expel the hydrogen sulfide. The solution, oxidized with hydrogen peroxide, is neutralized with sodium carbonate with two to three grams in excess and then boiled fifteen minutes, filtered and washed. The iron precipitate is dissolved in 1:1 nitric acid and reprecipitated as before. The filtrates are evaporated slightly and nitric acid is added, the solution being boiled to expel the carbon dioxide. The solution is neutralized with ammonium hydroxide, acidified with nitric acid and lead acetate solution is added, the nitric acid solution being neutralized with a concentrated ammonium acetate solution. After the solution has been heated for an hour, the lead vanadate is filtered off, dissolved, and reprecipitated as before.

The filtrates are evaporated and sulfuric acid is added to precipitate the greater part of the lead. The uranium and the remainder of the lead are precipitated by addition of ammonium hydrosulfide to the solution which has been neutralized with ammonium hydroxide. The precipitate is then dissolved in 1:2 nitric acid and fumed with sulfuric acid and then diluted, the lead sulfate being filtered off.

To remove the aluminum, the solution is nearly neutralized with ammonium hydroxide and ammonium carbonate is added in excess in the cold. After standing the aluminum is filtered off. A second precipitation is necessary in the presence of large amounts of aluminum. The filtrate is acidified with sulfuric acid and boiled to expel the carbon dioxide. The uranium is then precipitated in the hot solution

with ammonium hydroxide. The precipitate is removed by filtration, ignited, and weighed as the oxide. It may be tested for the presence of vanadium.

Procedure. Treat from two to five grams of the ore, according to the amounts of vanadium, iron, and uranium present, in a covered beaker, with 10 cc. of hydrochloric acid and allow the vessel to stand for 15 min. with occasional shaking. Add 5 cc. of nitric acid and heat on a steam bath. When the solution is quiescent remove the cover and evaporate to dryness. Add 3 cc. of hydrochloric acid and 5 cc. of water to the residue and allow this to stand for a few minutes on the steam bath. Stir occasionally. Dilute with warm water (25 cc.) and filter into a small beaker and wash the residue with warm water.

Some ores do not yield all the vanadium by this treatment, a small amount often remaining with the insoluble residue. To be sure that all of the vanadium is in solution, ignite the residue in a platinum dish, treat with 5 cc. of hydrofluoric acid and evaporate to dryness on a steam bath. Do not overheat the residue since it is not necessary to expel all of the hydrogen fluoride. Add 3 cc. of hydrochloric acid to the residue from the HF treatment and evaporate to dryness. Repeat this procedure to insure expulsion of the hydrogen fluoride. Treat the residue with 2 cc. of hydrochloric acid and 2 cc. of water and stir with a glass rod until any red crust that may be present is dissolved. Dilute the solution with water and filter into the main portion.

Pass hydrogen sulfide into the liquid to separate the copper, lead, and other metals of this group, filter, and boil the liquid to expel the hydrogen sulfide. Concentrate the liquid to 100 cc. If necessary oxidize the solution with an excess of hydrogen peroxide and then neutralize with sodium carbonate, adding two or three grams in excess. Boil the liquid for about 15 min. until the yellow uranate precipitate dis-

solves, leaving a brown precipitate consisting mainly of iron. Filter and wash the iron precipitate with water and reserve the filtrate. Dissolve the iron precipitate in the least possible amount of nitric acid (1:1) and add 10 cc. of hydrogen peroxide and neutralize with sodium carbonate with two grams in excess, and boil as before. Filter into the beaker containing the first filtrate. The iron precipitate may contain small amounts of vanadium; keep for subsequent treatment.

Evaporate the united filtrates from the iron precipitation to a volume of about 200 cc. and add 10 cc. of concentrated nitric acid and boil until all of the carbon dioxide is expelled. Neutralize the free acid by ammonium hydroxide until a slight permanent precipitate appears and then add 4 cc. of nitric acid for each 100 cc. of liquid. Add 10 cc. of a 20% lead acetate solution and enough concentrated ammonium acetate solution to neutralize the nitric acid present and substitute acetic acid for it. The object is to precipitate the vanadium as lead vanadate in an acetic acid solution. The ammonium acetate solution may be prepared by mixing 80 cc. of concentrated ammonium hydroxide, 100 cc. of water, and 70 cc. of glacial acetic acid.

Heat the liquid containing the lead vanadate precipitate on the steam bath for one hour or more, filter on a tight filter paper, and wash with warm water. Dissolve the precipitate in the least possible quantity of hot dilute nitric acid, neutralize as before, and add 3 cc. of nitric acid in excess. Add 2 cc. of lead acetate solution and repeat the precipitation of lead vanadate by adding ammonium acetate in excess. Filter and add the filtrate to the filtrate obtained from the first precipitation of lead vanadate.

Reserve the precipitate of lead vanadate for treatment described below. Evaporate the united filtrates from the lead vanadate to about 400 cc. Add 10 cc. of concentrated

sulfuric acid to separate the bulk of lead (from the excess of lead acetate) as lead sulfate, filter and wash the precipitate with cold water. Neutralize the filtrate from the lead sulfate with ammonia and add freshly prepared ammonium hydrosulfide until the solution is yellow and the uranium and the small amount of lead present are precipitated as sulfides. Warm the mixture on a steam bath until the sulfides settle. Filter and wash slightly with warm water.

Dissolve the precipitate in another beaker with dilute hot nitric acid (1:2), add 5 cc. of sulfuric acid and evaporate until fumes of sulfuric acid appear. Cool and take up with water, boil, and allow the precipitate of lead sulfate to settle until the solution is cold. Filter the precipitate off and wash with very dilute sulfuric acid.

Nearly neutralize the filtrate with ammonium hydroxide and allow the solution to cool (not warmer than 30° C.) and add powdered ammonium carbonate with about 2 gm. in excess to precipitate the aluminum. Allow the precipitate to settle, filter and wash with warm water. If the precipitate is bulky or is at all yellow dissolve it in a small amount of dilute sulfuric acid and reprecipitate with ammonium carbonate as before. Acidulate the filtrate from the aluminum oxide with sulfuric acid and boil thoroughly to expel the carbon dioxide.

Slightly alkalize the liquid with ammonium hydroxide while hot and heat on the water bath until the ammonium uranate collects and settles. Filter and wash with a 2% solution of ammonium nitrate. Do not allow the precipitate to become dry on the filter after the first washing. Dry the precipitate, ignite in a porcelain crucible and weigh as the oxide. Dissolve the precipitate in nitric acid and test it with hydrogen peroxide for vanadium and with ammonium carbonate for aluminum.

According to Davis it is important that all of the carbon

dioxide be removed by prolonged boiling for a half an hour. Hydrochloric acid may be used for neutralizing solutions instead of nitric acid. The aluminum precipitate should stand overnight before filtering; if not, the final residue of U_3O_8 will be contaminated. If the amount of the final precipitate is small a confirmatory qualitative test should be conducted. The process is slow, three days being required to finish a batch of analyses. An analyst who has had little experience with this method will obtain satisfactory results.

In 1928 C. N. Fenner investigated the methods of uranium analysis from the standpoint of their value as bases for age calculations. Fenner appropriately pointed out that there is considerable literature on the subject, but not much that is well systematized, nor formulated to meet the somewhat special requirement demanded in age determinations. Moreover, some of the methods appear to be applicable only under certain conditions, while their limitations are not stated in the descriptions given. While many methods are of a high order of accuracy others lead to results which appear improbable. Analytical accuracy is one of the most fundamental of the factors entering into the calculation of geologic age.

In Fenner's method for the determination of uranium and thorium in euxenite, polycrase, samarskite, and others only two or three grams of the powdered sample are required. To this five times as much sodium bisulfate is added and the mixture fused at bright red heat until the evolution of sulfuric anhydride nearly ceases. The product of fusion is cooled and an equal amount (grams for cubic centimeters) of sulfuric acid is added for the sodium bisulfate used. The mixture is digested for $1\frac{1}{2}$ hours while exposed to the fumes of sulfuric anhydride. The material is cooled and dissolved in cold water and allowed to stand over night, the precipitate from which is disregarded.

The solution containing the precipitate is divided into aliquot parts, on the basis of the sulfuric acid used in the digestion, in such a manner that one portion contains approximately 5 cc. of free sulfuric acid. The other portion is nearly neutralized with solid sodium carbonate and the two portions are reunited. The volume is increased to 450 cc. with water and the mixture is boiled vigorously for a half hour. The hydrolyzed precipitate of titanium, tantalum, and columbium oxides are allowed to settle on a steam bath and filtered. The precipitates are washed with hot water. As much as possible of the precipitate is removed with a platinum spatula and placed in a solution of 500 cc. of nitric acid diluted with 150 cc. of water. The solution is then boiled slightly and again filtered through the filter paper used before.

The two filtrates are kept separate and are evaporated to a smaller bulk. If a slight precipitate forms in the sulfuric acid solution this is disregarded. To this solution ammonium hydroxide is added in slight excess, and filtered, and then washed with a hot 2% solution of ammonium nitrate. The precipitate is dissolved in the nitric acid filtrate obtained from the digestion of the hydrolysis precipitate and the solution is set aside for additions.

The filtrate from the ammonium hydroxide is evaporated to a small bulk, cooled and another portion of ammonium hydroxide added. There may be a small amount of additional precipitate. Filter and wash with a small amount of cold 2% ammonium nitrate and dissolve the resulting precipitate in nitric acid and add to the previous nitric acid solution. The filtrate from the ammonium hydroxide treatment is rejected.

The combined precipitates of titanium, tantalum, and columbium obtained from hydrolysis are dried and ignited. They are then fused with five times their own weight of

sodium bisulfate and the subsequent procedure carried out as before. Finally, a third fusion and subsequent operations are performed. By this repetition the occluded uranium and thorium are carried down by the bulky hydrolysis precipitates and are brought into solution free from titanium, tantalum, and columbium.

The combined acid filtrates are boiled to expel any possible carbon dioxide. Ammonium hydroxide is added to increase the concentration to a greater degree, and then boiled. Filter and wash with a hot 2% solution of ammonium nitrate. Wash the precipitate from the filter into a gold or platinum basin and wash with dilute hot hydrofluoric acid (about 10 cc. acid) into the same vessel. The filter paper is ignited in a platinum crucible, in which the filter papers of the immediately subsequent fluoride filtrations are also ignited.

The filtrate from the ammonium hydroxide precipitation is evaporated to a smaller bulk and cooled. To the cold solution ammonium hydroxide is added. A small amount of white precipitate may form, which is filtered off and converted into the fluoride as before and added to the main portion.

The solution containing the precipitate of fluorides of thorium and rare earths is evaporated to a small bulk. The precipitate becomes granular. Dilute and filter, using a hard rubber funnel and wash with dilute hydrofluoric acid. The filtrate is used in the uranium determination.

The filtrate from the hydrofluoric acid precipitation of thorium and rare earths contains uranium, separation being apparently complete. This is evaporated with about 5 or 6 cc. of sulfuric acid in the fumes of sulfuric acid and then diluted with water. It is then neutralized with sodium carbonate, 2 or 3 grams being added in excess. The volume is increased to about 400 cc. and boiled for a few minutes. Filter and wash with a hot 2% ammonium nitrate solution.

Dissolve the precipitate in nitric acid. The precipitation is repeated by use of sodium carbonate. Filter and reject the second precipitate. Combine all of the sodium carbonate solutions and acidify with nitric acid. All of the carbon dioxide is expelled by boiling and a considerable excess of ammonium hydroxide is added, after which the solution is boiled and filtered.

Wash with a 2% solution of ammonium nitrate and reject the filtrate. Dissolve the precipitate of uranium in nitric acid and add ammonium hydroxide. To dissolve the uranium a solution of 3 gm. of ammonium carbonate in 5 cc. of ammonium hydroxide, and a small amount of water, is used. If a small amount of residue remains it is filtered off and rejected. The ammonium hydroxide and carbon dioxide are ejected by heating and the solution is slightly acidified with nitric acid and again boiled to expel the carbon dioxide. Any vanadium present may be removed as lead vanadate in an acetate solution. Metals of the hydrogen sulfide group may also be precipitated although they are hardly expected in materials suitable for age determinations. If hydrogen sulfide is passed through the solution, the solution is oxidized again before precipitating the uranium.

To the hot solution is added in slight excess and the precipitate filtered out and washed with a hot 2% ammonium nitrate solution. The residue is ignited strongly and weighed as U_3O_8 . The residue may contain a trace of silica and alumina so it is dissolved in warm 1:1 nitric acid and the small amount of residue filtered off, ignited and weighed, and subtracted from the U_3O_8 found.

For additional accuracy the presence of traces of iron, titanium, tantalum, columbium, and zirconium may be tested in the last nitric acid solution by converting into dilute sulfuric acid solution. To this a small amount of freshly filtered cupferron (ammonium phenylnitrosohydroxylamine)

is added. If any precipitate remains it should be ignited, weighed, and subtracted from the U_3O_8 found originally.

Volumetry

Nearly all methods for the determination of uranium by volumetric methods depend on the reduction and subsequent reoxidation with potassium permanganate solution. In 1867



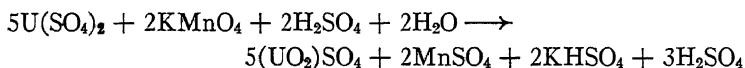
The Fisher Electrode Titrator permits titration of solutions without interference of the personal equation. The electrode titrator is one of a number of instruments which places heretofore somewhat subjective modes of chemical analysis on a more objective basis.

Belhoubek proposed this method for the estimation of uranium and since then it has been modified and used by many investigators. Volumetric analysis may best be summed as: Each investigator can secure good results by his own method but not by that of another (C. W. Davis, 1923). It appears

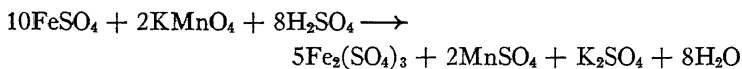
that experience is a fundamental factor in these determinations.

There is, however, a danger of over-reduction of uranium solutions, this having been pointed out as early as 1864 by Guyard. This investigator found that uranium reduced to below the tetravalent state by zinc, the results of analysis then being too high. Other investigators have obtained similar information. According to Follenius (1873) hydrochloric acid causes the reduction of uranium to below the tetravalent state. It is also pointed out that the presence of chlorine ions in uranium solutions may interfere with the volumetric determination of uranium; this, however, may be overcome by the addition of manganese sulfate.

Uranium differs from iron as regards reduction in that it is not reduced by hydrogen sulfide although if mercuric salts are added to uranium solutions reduction does occur by hydrogen sulfide. Permanganate solutions used in titrimetry of uranium may be standardized by iron, two molecules of iron corresponding to one molecule of uranium. The reaction which occurs in the titration of uranium sulfate is:



whereas the reaction in ferrous solutions is:



The reduction of uranium by zinc and sulfuric acid corresponds to the change of UO_3 to UO_2 .

The reduction of uranium solutions for titrimetric determination was discussed by Kern (1904) who enumerated the following methods:

1. The use of zinc and sulfuric acid and heating.

2. The use of zinc and hydrochloric acid and heating.
3. The use of aluminum and sulfuric acid.
4. The use of aluminum and hydrochloric acid.
5. The use of magnesium and dilute sulfuric acid.
6. The use of magnesium and hydrochloric acid.
7. The Jones' Reductor.
8. The Zimmermann-Reichardt method where a concentrated solution of stannous chloride is added to sufficient mercuric chloride. This method was found useless by Kern.

When hydrochloric acid solutions of uranium are reduced by zinc, aluminum, or magnesium, the reduction proceeds lower than the tetravalent state. Kern found that the state attained in some cases approached the subchloride, UCl_3 .

The most rapid determination of uranium is by reducing a sulfate solution with zinc and titrating with potassium permanganate. The titration is performed in an atmosphere of carbon dioxide. The reductions with zinc, aluminum, and magnesium, and with the Jones' Reductor, are complete and concordant with gravimetric methods (Kern).

In 1911 Ibbotson and Clark poured a solution of uranyl sulfate, in 2-5% sulfuric acid, into 50 gm. of 20 mesh zinc and heated the mixture until it became a dark brown color. After cooling it was rapidly filtered and the zinc washed with cold water. Air was then passed through the solution for one minute and the resulting solution titrated with standard potassium permanganate.

Campbell and Griffin (1909) determined uranium in the presence of vanadium by first reducing with SO_2 and then titrating with potassium permanganate, the uranium not being reduced. The solution is then warmed with an aluminum spiral, which reduces both the uranium and the vanadium, and retitrated with potassium permanganate. The aluminum spiral is washed with ferric alum to prevent oxidation

of the vanadium. The method is stated to be uncertain in the presence of large amounts of vanadium.

Newton and Hughes (1915) determined uranium, in the absence of iron, by titanium sulfate. An excess of titanium salts were oxidized with Bi_2O_3 and the remaining bismuth salts were filtered off, the uranium then being titrated with potassium permanganate.

Auger (1912) reduced uranium in the presence of iron with zinc amalgam. Titration is performed with a ferric salt using potassium thiocyanate as an indicator. In the presence of iron and titanium an excess of sodium tartrate is added and the mixture reduced by a titanous salt. Nitro-indulene is used as the indicator.

Ledoux and Company (1916) reduced uranium by zinc amalgam in a Jones' Reductor and shook the solution in an excess of air for one minute before titration with 1/20 normal potassium permanganate, one-half cubic centimeter being subtracted for the end-point and reduction error.

Mohr (1893) determined uranium volumetrically by titration of the acetate solution with sodium hydrogen ammonium phosphate, this being added drop by drop until brought into contact with fresh potassium ferrocyanide failed to produce the characteristic brown coloration.

Recent investigations into titrimetry by more advanced methods have been evolved from greater knowledge of the actual mechanisms which occur in reduction and oxidation processes. These have enhanced the value of volumetric methods for estimation of uranium immensely. It would appear that a line of demarcation exists between the volumetric studies performed several decades ago and those which have been performed in the last few decades. This line of demarcation would consist of precision based on sound knowledge of actions which actually occur in solutions.

The volumetric determination of uranium was studied in 1936 by M. Axt. The procedure in this test is to add 100 ml. of the solution containing uranium in the form of 0.5 gm. uranyl salt to 10 to 15 ml. of 2% sulfuric acid and filter. The filtrate is added to zinc amalgam (15 gm. of zinc for 500 gm. of mercury) and agitated for 3 minutes. This is then filtered through cotton and air passed through for 5 to 10 minutes. Ten milliliters of 20% ferric sulfate solution are added and titration with standard 0.1 N. potassium permanganate solution performed.

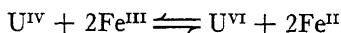
The United States Bureau of Mines has a convenient method for commercial analysis of ores such as carnotite and other vanadiniferous uranium ores. Their technique was derived from previous work of Finn in 1906; Engle in 1908; Ledoux and Company in about 1916; and, from the work of Moore and Kithil in 1916. In the official mines technique the ore is treated with nitric acid, fumed with sulfuric acid to remove the nitric acid, and then diluted and treated with hydrogen sulfide to remove the second group elements. To the boiled solution hydrogen peroxide and sodium carbonate are added and the mixture boiled and filtered to remove the iron and aluminum.

The iron-aluminum precipitate is dissolved in acid and again precipitated to remove the occluded uranium. To the filtrates ammonium hydrogen phosphate and sulfuric acid are added and, after boiling off the carbon dioxide, the solution is first made alkaline with ammonium hydroxide and then slightly acid with acetic acid. The uranium phosphate precipitate is filtered off, dissolved in sulfuric acid and again precipitated to remove the occluded vanadium. The final phosphate precipitate is dissolved in sulfuric acid and tested for vanadium by hydrogen peroxide. The solution is oxidized with potassium permanganate and reduced in a Jones' Reductor and agitated to oxidize any over-reduction which

might have occurred. Titration is conducted with standard potassium permanganate solution.

Between 1925 and 1933 considerable investigation on the volumetric determination of uranium with potassium dichromate as a reagent was performed. In 1925 Lundell and Knowles, and in 1931 N. H. Furman and J. C. Schoonover demonstrated that reduction of hexavalent uranium in either hot or cold solutions leads to the formation of tetravalent uranium with an undetermined amount of trivalent uranium. The trivalent uranium can be oxidized easily to the tetravalent state by treating with a stream of air for several minutes. It was also found that tetravalent uranium is quite stable in contact with air at room temperatures provided the proper pH (acidity) is maintained.

In 1932 I. M. Kolthoff and J. J. Lingane corroborated these results. They found that tetravalent uranium can be titrated with accuracy by use of potassium dichromate as a reagent and diphenylamine sulfonate as an indicator. A number of other related substances can be used in place of the diphenylamine. It was found, however, that the direct titration of tetravalent uranium by use of either diphenylamine or diphenylamine sulfonate as indicator is not entirely feasible because of the extreme slowness required for the development of the color at the end-point. Experiments showed that uranyl ions inhibit the speed of oxidation of these indicators. This difficulty was overcome by the addition of an adequate amount of ferric ion which acts as follows:



The ferrous ion is a powerful catalyst in the oxidation of the above indicators to the colored forms, a sharp end-point being obtained in the titration when an excess of ferric ions are present. The diphenylamine sulfonate produces a more

satisfactory result than either diphenylamine or diphenylbenzidine and the former compound is recommended in the titrimetry of uranium.

The titrimetry of uranium has been studied by Ewing and Eldrige (1922). In this work it was shown that the electrometric titration curves for uranium and potassium permanganate, and potassium dichromate have two inflection points. The first inflection point indicates complete oxidation of the trivalent uranium ion to the tetravalent uranium ion. In the second point complete oxidation to the tetravalent form is indicated.

In 1922, Gustavson and Knudson, and in 1923, Muller and Flatt titrated uranium electrometrically but apparently failed to note the first inflection point. Kolthoff and Furman (1926) correctly pointed out that the presence of carbon dioxide and the correct pH (acidity) is required in order to obtain a titration for trivalent uranium.

In 1931 Dwight T. Ewing and M. Wilson studied the electrometric titration of uranium by ceric sulfate. These investigators found that when a hot acid solution of uranium sulfate is reduced in a Jones' Reductor and is titrated in an atmosphere of nitrogen with ceric sulfate as an oxidizing agent two end points are obtained. The amount of uranium oxidized between the two end-points corresponds exactly to the amount of uranium present with the best result being obtained with a 2% sulfuric acid solution of uranium sulfate.

Uranium acetate in hydrochloric acid can also be titrated but sharper end-points are obtained for the titrations in sulfuric acid, and less time is required for the e.m.f. to reach equilibrium than when hydrochloric acid solution is used. Ferrous ammonium sulfate is added to the reduced 2% uranium sulfate-sulfuric acid solution and three end-points are obtained, i.e., (I) when trivalent uranium is oxidized to tetravalent uranium, (II) when tetravalent uranium is oxi-

dized to hexavalent uranium and, (III) when ferrous ions are oxidized to ferric ions.

Electrolytic Procedure

The two classical methods for electrometric titration of solutions are potentiometric and conductometric titration. Potentiometric titrations are characterized in that the potential of a suitable indicator electrode is measured during titration and the end-point is noted by more or less of a pronounced change in the potential on addition of a small amount of the reagent. In conductometric titration the electrical conductance of the solution is measured during the technique and the end-point is found graphically as the point of intersection of the lines giving the changes of conductance before and after the equivalence point. Kolthoff has added another method to these, being called amperometric titrations.

Britton (1934) has mentioned the conductometric analysis of uranium. For example, van Suchtelen and Itano claim that a solution of diammonium phosphate can be conductometrically titrated with 0.25 N. Uranyl acetate. It would appear that this technique might be used in reverse to titrate uranyl salts in dilutions of the magnitude of that used for the estimation of the diammonium phosphate. Furthermore, Dutoit (1910) used uranyl nitrate to titrate arsenate ions in the presence of sodium acetate. The readings obtained in this titration are, however, not readily constant and the procedure is time-consuming. Conductometric analysis was used by Britton and Young in their studies on evidence in favor of the existence of the uranyl ion.

In 1934 I. Kitajima estimated 8-hydroxyquinoline and anthranalic acid accurately by potentiometric titration with hydrobromic acid. This determination can be made in the presence of copper, cadmium, aluminum, manganese, zinc, iron, nickel, cobalt, calcium, magnesium, or uranium. An-

thranalic acid may be determined in the presence of nickel, copper, zinc, and cobalt. It follows that an indirect determination of these metals is possible by the titration of 8-hydroxyquinoline or anthranalic acid precipitates in the presence of hydrochloric acid.

In a paper presented before *The Electrochemical Society* (1939) I. M. Kolthoff discussed amperometric titrations. In amperometric titrations the current passing through the titration cell is measured. A high degree of accuracy accompanies titrations on extremely dilute solutions. Foreign, indifferent electrolytes whose presence is harmful in conductometric titrations do not interfere in amperometric titrations. Their presence is desirable to suppress migration currents. The titrations can be carried out rapidly because the end-point is obtained graphically and only several measurements before and after the end-point are required. Characteristic current-voltage curves for uranium may be of value in studies where other methods do not yield satisfactory results.

The determination of uranium by electrolytic means was performed by Classen in 1885. In this the uranium was precipitated as the hydroxide from the oxalate solution. Other investigators have used essentially the same technique with, instead of the oxalate solution, solutions of acetates, formates, nitrates, and sulfates.

In an acetic acid solution, with a current of $N.D. \frac{5}{40} = 0.18$ ampere, at 3 volts potential, the uranium may be precipitated provided the temperature used is 70° C. This is ignited to the oxide. An accuracy of 0.3% is claimed for this method. Kern has studied the electrolytic means for the determination of uranium.

A. Schleicher (1935) electrolyzed 0.1 cc. of uranium solution with a feeble current on the lid of a platinum crucible,

this consisting of the anode. The cathode consisted of a copper wire. After electrolysis the lid was removed and replaced by the same material as the cathode, the residue and solution evaporated in the electric arc and the vapor obtained examined spectroscopically. The electrolysis is carried out first in acid and then in ammoniacal solution. The test is regarded as exceedingly delicate.

Buell's test is one which may be regarded as electrolytic. The procedure is to add purified zinc moss or plate to a concentrated solution of the ore which involved nitric acid for the extraction of the uranium. In a slightly acid solution a yellow coating is formed on the zinc. This coating consists of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$.

The yellow deposition in Buell's test may be positively confirmed as uranium by its fluorescence. This is desirable since other elements may form yellow coating on zinc. Under short wavelength ultraviolet radiation (2537 A.U.) the substance should have the characteristic uranium yellow-green fluorescence. The fluorescence of the residue is not always fully observed until spotting with hydrochloric acid is performed. This treatment renders the coating fluorescent, acid serving to alter it to a fluorescent uranyl entity. Additional information on fluorescence analysis is given in a section of this chapter which follows.

Colorimetry and Nephelometry

Reactions in uranium chemistry which produce a cloudiness, color, or turbidity may usually be measured by colorimetric or nephelometric methods. If the reaction occurs under standard conditions so that the turbidity is always of the same nature, and the intensity depends only on the amount of one of the substances, i.e., the uranium, then the method may obviously be used conveniently for the determination of the substance. In colorimetric determinations of uranium, as

well as in other elements, the reaction must conform to certain requirements. The haze must be reproduceable in all respects. Thus, if certain working details are adhered to, the particles of the haze must always be the same in number, size, and distribution. As a corollary to this the nature of the haze must not be modified by points of difference (by the presence of materials) which may exist between the sample and the standard.

The haze should be reasonably stable and should not change in color, intensity or distribution while the match is being made. To this end protective colloids may be added (e.g., NaCl in the ferrocyanide test), or the pH value suitably adjusted (e.g., in hydrogen sulfide hazes). The reaction should be sensitive, i.e., a small amount of uranium should produce a pronounced haze (e.g., the reaction(s) of uranium with amines). The haze should be insoluble in its surrounding medium.

It follows, therefore, that practically all wet reactions which produce precipitates (hazes) or colors may be adapted to determination by colorimetric methods. Colorimetry, formerly a means of analysis which was somewhat restricted by the human equation is now on a par with other modes of analysis in that it may be performed entirely by instrumental means with a great deal of accuracy.

The chromotropic acid test of N. A. Tannaer and A. Gintsburg (1938) may be adapted to colorimetry. In this chromotropic acid, 1,8-dihydroxynaphthalene-3,6-disulfonic acid, is the reagent. The procedure is to treat the specimen with a slight excess of stannous chloride, SnCl_2 , while heating to boiling.

The filtrate is added to the chromotropic acid reagent. Titanium forms a cherry-red color or a weak brown color depending on the concentration. The addition of nitric acid decolorizes the solution. The solution containing uranium is

treated with an excess of ammonium hydroxide and heated to boiling. It is then filtered and the residue treated with 2 to 5 cc. of acetic acid and washed several times with the filtrate to dissolve the ammonium uranate. If the filtrate is colorless add potassium ferrocyanide. With uranium the characteristic red-brown coloration is obtained. Iron must be separated previously since it interferes with the coloration.

As early as 1893 Bruttini suggested that the depth of color produced when potassium ferrocyanide reacted with uranium solutions could be used as a means for the estimation of uranium. This method may be used with a colorimeter.

Snell (1921) and others have discussed the colorimetric analysis of uranium by use of potassium ferrocyanide. Interfering metals, except aluminum, must be absent, these being separated by the procedures described in the first part of this chapter. The technique may be used for specimens containing 0.4 to 1.2% uranium as the oxide. The balancing method is used, this being dependent on comparison with known solutions.

Muller (1919) used a method for the colorimetric estimation of uranium. The test is based on the colors produced when aliphatic α -hydroxy and keto acids, and aromatic hydroxy carboxylic acids or higher phenols are added to uranyl solutions.

The most practical of the tests mentioned by Muller is that with *o*-hydroxybenzoic acid which forms a red salt with uranyl salt solutions. The method is accurate to 7% and is not interfered with by neutral salts although large amounts of the following must be absent: mineral acids, iron salts, organic solvents, and organic acids. The sample is used in the form of the nitrate and excess mineral acids are buffered by sodium acetate and boiled to expel the free acetic acid formed.

The procedure is to add 25 cc. of a 2% solution of sodium

o-hydroxybenzoate to an equal amount of the specimen in solution in the form of uranyl nitrate. Simultaneously, 25 cc. of a standard are diluted with the reagent. Comparison is made by balancing; the standard containing 0.1 mg. of uranium in every cc. A standard solution of uranium may be prepared by dissolving 2.11 gm. of uranyl nitrate ($6\text{H}_2\text{O}$) in 100 cc. of water, every cc. of which contains 10 mg. of uranium.

The Das-Gupta test may be used colorimetrically. Tannic acid, gallic acid, and resorcylic acids produce a brown coloration with uranium solutions. The addition of sodium acetate intensifies this coloration while acid salts must be absent as well as excesses of acetic, nitric, or hydrochloric acids, these being neutralized or evaporated. Should the precipitate formed by tannic acid, which is the most delicate, become colloidal, gallic acid is substituted. Sodium acetate often causes colloidal action occur with tannic acid.

The procedure is to use 25 cc. of the sample and 2 cc. of fresh 1% tannic acid solution and mix with 3 cc. of 5% sodium acetate solution. This is then diluted with water and mixed thoroughly. Comparison is performed with a standard by the balancing method. Exposure to air affects the colors.

X-ray Spectrography

One of the superior methods for determination of the identity of a mineral is that of X-ray spectrography. The commonly used procedures in this form of analysis are of two kinds. In one, a single crystal is studied; the results being in the form of one of a possible number of different X-ray spectrograms, i.e., depending on the method, e.g., the Laue Method or the Rotation Method. In the other, the specimen is finely powdered and a diffraction pattern is obtained.

Diffraction analysis has several advantages over the single crystal method in that many substances are difficult to obtain in the form of a single crystal large enough to study. The interpretation of single crystal spectrograms is often exceedingly difficult. The powder pattern is especially suited for general use. Small amounts of fine powders or crystalline aggregates may be analyzed for crystalline structure.

The developments in the diffraction of X-rays by powders as a form of analysis have been discussed by George L. Clark (1940) in detail. The discovery of the powder method has been one of fundamental importance to the science of X-ray spectrography. In Europe, Debye and Scheerer used the procedure at about the same time that it was being developed in America by Hull.

George L. Clark and S. T. Gross, in collaboration with the present writers, first prepared standard "finger-print" patterns (X-ray powder patterns) of radioactive minerals by relatively new techniques. The investigations, conducted in 1941, included the three main types of radioactive minerals, i.e., Type I—The Primary Uraninites such as pitchblende and uraninite; Type II—The Columbo-tantalates such as columbite and tantalite; and, Type III—The Secondary Uraninites, those which are the alteration products of Type I minerals such as autunite, schroëckingerite, gummite and others.

The investigations open an entire field since the patterns may be just the beginning of a whole series of standard mineralogical patterns. The technique of separation used in the present investigations, for a typical specimen, may be effectively extended to other varieties of minerals. The secondary uraninites were hand-picked in ultraviolet radiation (wavelength = 2537 A.U.) if fluorescent. The non-fluorescent matrix or differently-fluorescent associated minerals can be easily separated from the standard specimen.

As would be expected, in fine powders the particles are arranged chaotically. However, when enough particles are present a strong reflection of X-rays occurs from one set of parallel planes at one angle whereas another set of planes at another angle produce a different reflection. The effect of this is to produce a series of concentric rings on a photographic plate after the X-ray beam has passed through the powder specimen. Each ring is uniformly intense and corresponds to one set of planes. A section of this concentric ringed photograph has the appearance of a line spectrum.

The immense value of these spectra is that only definite lines in a specific pattern correspond to a pure crystalline substance like a finger-print, hence the term "finger-print patterns" for powder diffraction patterns. It follows, therefore, that the pattern of a known pure crystalline compound may be compared with the pattern of an unknown crystalline compound. This form of analysis may be adapted to the identification and characterization of uranium minerals since it is well suited for the study of complex substances.

In general, the limits of detection of a crystalline substance in the presence of other crystalline substances may be as low as a fraction of one per cent. Specimens as small as fifty milligrams may be used for preparation of the spectrogram. Most effective results, however, are obtained with greater quantities, these being better suited to quantitative analysis by intensity measurements.

The procedure in "finger-print analysis" is to insure random arrangement of the particles. This is done by powdering the specimen so that it will pass through a 200 mesh screen, i.e., smaller than 10^{-3} cm. Specimens of minerals should be as *typical* of the species as possible and should be obtained by the most careful means possible if they are to be used for standards. Handpicking under the microscope or specific gravity methods aid in isolating representative material.

Electroscope and Counter Determination

Electroscope and counter detection of uranium present a number of advantages not possessed by most of the other procedures. Radium, a powerful radioelement, is always associated with uranium in nature. By means of the presence of radium the detection and determination of uranium is performed with greater ease since both emit ionizing radiations by which their existence in a specimen may be verified. It will be noted, however, that thorium may cause the discharge of an electroscope or Geiger-Mueller Counter.

The radioactive method for ores has been discussed by many investigators. C. W. Davis emphasized that an unusual case exists. This consists of the determination of one element through the determination of another since uranium and radium always exist together in a ratio which is generally constant (see Boltwood's Constant).

The method of Moore and Kithil (1916) is based on the radioactive principle and may be used for the approximate estimation of uranium in carnotite. In the test a known (analyzed) sample of ore is used as the standard, this being compared with the unknown, both of which should be as nearly alike as possible on the basis of physical properties. The determination of the amount of uranium is based on the time required for the charged leaf of an electroscope to pass a certain number of graduations on a scale. A sample of uniformly ground ore of a definite surface area and weight is placed at a fixed distance from the conducting plate of the system and its activity noted. Finally, the analyzed sample is determined in the same way. Aside from the deduction of the natural leak of the instrument, the two activities may be directly compared and the amount of uranium determined in the unknown in terms of the known, a small variation being allowed for error.

In the following table the various radioelement ratios are given. Attention is directed to the uranium ratios with other elements. Uranium may be determined indirectly on the basis of the analysis of the other element. It must be remembered that in several of these systems, however, equilibrium may not exist. This might be due to several conditions but the important fact is that the proportion of uranium, or other radioelement, to the element by which the determination is indirectly being made does not exist as it does in the majority of instances. Dakeite is a mineral in which the equilibrium between uranium and radium does not conform to Boltwood's Constant.

RADIOELEMENT RATIOS

<i>Radioelement Ratio</i>	<i>Value</i>	<i>Reference</i>
Uranium: Radium.	3.40×10^{-7} ; every 1000 kilos of U in ore contain 0.34 gm Ra.	See N. Lange's <i>Handbook of Chemistry</i> , Sandusky, Ohio (1937). (Boltwood's Constant).
Uranium:		
Thorium.	2.8 (average); 2.3 in acid eruptive rocks; 2.1 in medium acid rocks; and, 1.5 in basic rocks. The 2.8 is for sedimentary (not limestone) rocks.	Hans Pettersson, <i>Anz. Akad. Wiss. Wien., math-naturv. Klasse</i> , 127 (1939); <i>Chem. Zentr.</i> , 2, 3382 (1938).
Uranium:		
Actinium.	Constant in that 1000 kilos of U in ore contain 0.06 mgm Ac.	Bruner and Schlundt, <i>Jour. Phys. Chem.</i> , 38, 1183 (1934); vide supra.
Uranium:		
Vanadium.	3.09 (theoretical) in carnotite or tyuyamunite.	Paul Tyler, <i>Bur. Mines I.C.</i> 6312 (page 54) 1930.

RADIOELEMENT RATIOS—(*Continued*)

Uranium:

Protoactinium. . . $0.285-0.290 \times 10^{-3}$; in Tchen Da Tchang,
every ton of U in ore *Ann. chim.*, **2**, 186
0.27 gm Pa exists. (1934); vide supra.

Uranium: Ionium. . . 0.53 (assumed), the *Compt. rend.*, **199**, 412
value of AcU being (1934).
about 4.12% of the
U.

Actinium: Ionium. 0.243 (average) Same as U:Io

Thorium:

Mesothorium. . . 0.531×10^7 McCoy and Hender-
son, *Jour. Amer.*
Chem. Soc., **40**,
1316 (1918).

Spot Tests and Organic Precipitants

Turmeric is a reagent which may be used for the detection of uranium. Fresh turmeric paper turns an orange-brown color in the presence of uranyl ions. On spotting turmeric paper, after the brown uranyl coloration has been produced, with sodium carbonate solution a violet-black coloration forms. The original yellow color of turmeric may be restored by treatment with hydrochloric acid.

The turmeric test was first proposed by Zimmermann, one of the pioneers in the field of uranium chemistry. The test has been extended by the present writers by the application of other reagents after reaction with uranyl ions and also by examination in ultraviolet radiation. In the fluorescence analysis of turmeric long wavelength radiation is used since organic materials are best excited by this type of light. In the accompanying table results of this sort are given. The organic substances in the list have been applied after the

turmeric was colored brown by uranyl ions. The appearance of untreated turmeric paper is also given in the list for purposes of comparison.

A fresh isopropanol solution of turmeric forms a deep red coloration with uranyl salts (when in solution—not on paper). The addition of 2-amino-2-methyl-1,3-propanediol causes a deep blood-red grainy precipitate to form.

REAGENT EFFECTS OF URANYL NITRATE IN TURMERIC PAPER

<i>Reagent</i>	<i>Color</i>	<i>Fluorescence</i> (<i>E</i>) λ = 3650 A.U.*
Dry Test Paper.....	Yellow.....	Yellow
Wet Test Paper.....	Yellow.....	Bright Yellow-green
Uranyl Nitrate.....	Orange-brown.....	Scarlet
Isopropylamine.....	Dark red.....	Crimson
Methyl formate.....	Orange.....	Purple
Methyl lactate.....	Orange.....	Light purple
Ethyl borate.....	Light orange.....	Cream
Dimethyl phthalate.....	Light orange.....	Greenish
Dibutyl tartrate.....	Light orange.....	Blue-green
Dibutyl sebacate.....	Light orange.....	Blue-green
Butyl stearate.....	Light orange.....	Red with bluish
Tributyl citrate.....	Dirty yellow.....	Red with brownish
Tributyl phosphate.....	Orange.....	Red

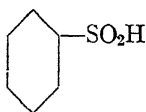
* Compare the use of this exciting wavelength with the data in the table of Wet-Dry Fluorescence of Uranyl Salts in the Section on Fluorescence Analysis.

P. N. Das-Gupta (1929) used gallic acid and tannin for the detection and determination of uranium (cf. section on colorimetry). According to W. Schoeller and H. Webb (1936) precipitation of uranium by the tannin series is not practical. Tannic acid has been used for the determination of uranium in tissues by L. Guisande (1930).

Additional investigation by Das-Gupta showed that tannic acid, gallic acid, or resorcylic acid when followed by sodium

acetate produce a marked coloration with uranyl ions. These reagents appear to be more sensitive than the sodium salicylate test. The best results are obtained with gallic acid in a neutral solution containing the uranyl ions, to which 2 cc. of gallic acid solution and 0.1 cc. of 0.5% sodium acetate solution have been added. In 10 cc. of test solution as little as 23 mg. of uranium per liter may be detected.

Benzene sulfinic acid has been suggested for the quantitative determination and separation of uranium from other metals by Feigl and Lenz (1940). The reagent has the structure:



where the action which occurs with uranium is that, in the insoluble benzene sulfonates the phenyl group, through its system of conjugated double bonds, is coordinated to the ion. The product is dried and weighed as the sulfinate.

The analysis of uranium is effectively accomplished by use of cupferron as the reagent. J. Holliday and T. Cunningham (1923) have used this method. Tetravalent uranium or uranium which is in a lower state of oxidation than U^{IV} can be completely precipitated with a freshly prepared solution of cupferron. The reagent must, however, contain 2 to 8 cc. of sulfuric acid for every 100 cc. of test solution. The cupferron salt may be ignited to U_3O_8 and the uranium determined gravimetrically.

If the amount of sulfuric acid in the solution is less than 4 cc. for every 100 cc. the aluminum, and probably the phosphorus will be carried down with the uranium. If the acidity exceeds 8 cc. per 100 cc. the uranium will not be completely precipitated. Sharp separation of uranium from aluminum,

zinc, calcium, magnesium, and phosphorus occurs if the acidity is maintained at an optimum of 6 cc. per 100 cc.

A large amount of convincing evidence was presented by the above investigators to prove that uranium and vanadium can be precipitated with satisfactory accuracy even in the presence of widely varying amounts of iron, aluminum, calcium, magnesium, and phosphorus. The procedure in assay of uranium by cupferron follows.

Precipitation of the vanadium and iron from a 12% sulfuric acid solution in which the uranium, vanadium, and iron are present in higher states of oxidation. Uranium, aluminum, calcium, unless present as the relatively insoluble calcium sulfate, magnesium, and phosphorus pass with the filtrate after filtration. The vanadium can be determined in this by the usual analytical methods. The cupferron may be decomposed by treatment with nitric acid and evaporating.

The uranium is reduced by means of a Jones' Reductor and zinc sulfate which is introduced into the solution after passing through the reductor does not materially interfere with subsequent reactions. For methods of reduction see Kern's work in the section on volumetric analysis.

Precipitation of the uranium from a 6% sulfuric acid solution with cupferron followed by filtration and washing to remove the aluminum, zinc, calcium, magnesium, and phosphorus.

Finally, the procedure is to ignite the organo-uranium compound to the oxide. The uranium content is checked by fusing with potassium pyrosulfate and dissolving the fusion product in sulfuric acid and passing the solution through a Jones' Reductor after which the value is checked by titration with standard potassium permanganate solution.

A new reagent has been introduced for analysis of uranium. V. Kuznetsov (1940) found that uranium produces a violet coloration with anthraquinone-1-azo-4-dimethylan-

line hydrochloride. The reagent is prepared by dissolving the chemical in alcohol and acidifying it with hydrochloric acid. Filter paper which has been impregnated with the reagent will detect gamma quantities of uranium. The test has been used for a number of other elements and is most sensitive in a solution saturated with sodium chloride.

Quinaldic acid is a reagent useful in the determination of uranium. The quinaldic acid reagent is prepared by solution in sodium hydroxide or ammonium hydroxide, this on addition of uranyl salts forms a golden insoluble precipitate which is insoluble in acids (cf. solubility aspects of uranates).

According to Gemuth and Mitchell (1929) sodium alizarin sulfonate (alizarin-S) forms a deep-violet precipitate with uranyl salts. The present writers have found that often, however, other alizarin salts of a slightly different nature form a blue lake. According to C. Lee (1940) this test is troublesome in that it can only be applied to comparatively pure salts obtained from solution and separation operations. Alizarin lakes with uranium do not have a characteristic fluorescence. The structure of alizarin lakes which involve uranium has been discussed in the previous chapter.

Insoluble coordination compounds are formed when a divalent metal or ion reacts with 8-hydroxyquinoline (oxine). These are characterized by a definite composition, stability, and crystalline structure. The uranyl salt of 8-hydroxyquinoline provides the basis for the determination of uranium. In 1933, F. Frere precipitated $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_6\text{NOH}$ from uranyl salts by 8-hydroxyquinoline without water of crystallization. It was found that one molecule of the 8-hydroxyquinoline is lost on heating to 200°C . The exact structure of this material has been referred to in the previous chapter.

Two other hydroxyquinoline salts have been used in the determination of uranium. 6-hydroxyquinoline was used by

J. Eisenbrand and 9-hydroxyquinoline by other investigators. The salts formed by these reagents are very similar to the 8-salt described above.

Bead Tests

A number of exceedingly useful bead tests may be used for the detection of uranium. The usefulness of bead tests is extended when it is realized that a positive bead test indicates the presence of radium also. In one bead test as little as 10^{-10} gm. uranium may be demonstrated and measured. Amounts of this magnitude are well below the limits of so-called sensitive means of analysis such as the spectroscope.

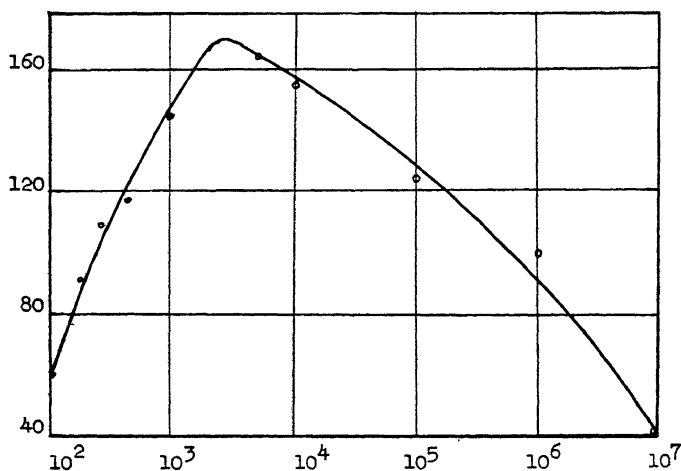
A clear bead is prepared by fusing borax or other salt on a cleaned loop of platinum wire. After preparation the bead is touched to the dry unknown and again held in the flame. Colors develop in respect to the part of the flame used, e.g., the outer part of the flame is the oxidizing region and the inner cone is the reducing region.

BEAD TESTS

<i>Color</i>	<i>Borax</i>		<i>Microcosmic Salt</i>	
	<i>Oxidizing Flame</i>	<i>Reducing Flame</i>	<i>Oxidizing Flame</i>	<i>Reducing Flame</i>
Green.....	Nil.....	Hot and Cold.....	Cold.....	Hot (W)
Yellow.....	Hot (Fe, V).....	Nil.....	Hot (Co, Fe).....	Nil

With borax in an oxidizing flame a yellow bead is obtained while hot but after the bead cools it becomes colorless. This bead can be flamed enamel yellow. In the reducing part of the flame a green bead is formed which can be flamed black but not enameled. With fusible phosphates an emerald-green bead is obtained in the reducing flame and in oxidizing flames a yellow bead is formed which cools to a yellow-green color. The accompanying table gives additional information on the color of beads in white light.

The inspection of beads in ultraviolet radiation greatly enhances their value in uranium analysis. The sensitivity of fluorescence bead tests for uranium was revealed in the studies of Nichols in 1912. It was found that a vivid yellow fluorescence may be produced by one molecule of uranium in 10,000,000 of sodium fluoride, in the form of a bead, and still be easily measured. At a dilution of one molecule of uranium to 2000 molecules of sodium fluoride optimum brightness occurs. The accompanying graph shows this effect. In order to represent the great range covered by the measurements, the curve is plotted to a logarithmic scale for the abscissae, where the abscissae are molecules of solvent to one molecule of the activator (UO_2F_2).



Nichols' curve for the optimum, showing the effect of uranium (as UO_2) in fused beads of sodium fluoride.

The data of Nichols was used in 1927 by Papish and Hoag to detect traces of uranium salts which could not be effectively demonstrated by other tests. These investigators

fused uranium salts with potassium metaphosphate, borax, sodium or calcium fluoride and obtained a bead with an intense lemon-yellow fluorescence. The investigators relied upon sodium fluoride for their tests and obtained results which were somewhat faulty in that columbium was found to produce similar effects.

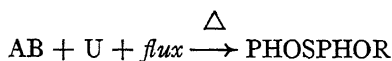
Specificity is obtained by use of potassium fluoride since other elements do not interfere with the fluorescence although the intensity is reduced considerably. The present writers have pointed out previously in another work that this test provides an indirect means for the demonstration of radium in minerals.

At about the same time that the work of Papish and Hoag was being conducted studies were performed by H. Eitel for the detection of uranium in cases of poisoning. Eitel used bead tests in his research and found it possible to demonstrate as little as one part of uranium in 500,000 parts of kidney ash. In cases of poisoning by uranium the kidney is the seat of deposition for the poison, a fact of importance since ashing the suspected kidney and fusion of a small amount of the ash into a bead will reveal the presence of amounts of uranium which may have caused injury or death to the organism.

In 1935 significant developments in bead tests for uranium were revealed by the investigations of F. Hernegger, et al. By use of spectrographic and microphotometric methods in conjunction with fluorescence analysis, the luminescence of sodium fluoride beads which contained traces of uranium was measured. These investigators found that as little as 10^{-10} gm. of uranium could be measured with precision. The striking degree to which this test was applied is shown by the studies on the uranium content of sea water. Experiments demonstrated that sea water contains from 0.36 to 2.3×10^{-6} gm. of uranium per liter.

The numerous studies in fluorescence analysis by H. Goto (discussed elsewhere in this chapter) demonstrated that the bead test is effective with as little as 0.02 gamma of uranium provided a sodium fluoride bead is used.

Fluorescent uranium beads are phosphors. And many fluorescent uranium minerals are phosphors. Both of these come under the classification of solid solutions. They consist of a system in which a small amount of uranium is intimately associated. This trace or impurity of uranium in a luminescent substance is called an activator and the large amount of inert substance acts as a flux or constitutes a solvent. Artificial compounds of this sort, such as beads, are termed phosphors which may be represented in the case of U-phosphors by:



where A may be Ca, Ba, Sr, Mg, Be, Na, K, Rb, Cs, Cd, Li, or Zn. A is the cation and is associated with the anion (B) which may be: sulfide, oxide, selenide, telluride, tungstate, silicate, carbonate, cyanide, hydride, thiocarbonate, thiosulfate, or thiocyanate. The flux may be the sulfate, borate, thiosulfate, mono or diphosphate, chloride, fluoride, or others used either singularly or mixed of the following: Na, K, NH_4 , Ba, Li, Be, Mg, or Ca. Generally, the term *base* is used to include both AB and the flux since both are not necessarily required for the completion of a phosphor, especially in beads. Organo-uranium phosphors, those which involve solid solution of uranium in an organic base, have not been studied extensively. NaUF is the typical notation used for a phosphor containing uranium.

A definite relationship exists between the concentration of an activator, e.g., uranium, and the intensity of fluorescence. If the concentration of uranium in beads passes a

certain optimum the intensity of fluorescent light will decrease considerably. Nichols' curve for the optimum of uranium in sodium fluoride is shown in the graph in this section. In 1909 Bruninghaus used the following relationship

$$I = Kxe^{-kx}$$

for the intensity of light that escapes from a material as correlated with x , the concentration of uranium in its solvent. This relationship has not received a great deal of experimental verification although F. Perrin's relationship

$$\phi = \phi_0 e^{-kc}$$

is in the same category, being for solutions. ϕ_0 and ϕ are the initial and observed intensities of fluorescence, respectively, and c the corresponding change in concentration, k being a constant of the latter.

The generally accepted characteristic color of uranium is lemon-yellow. Attention is directed, however, to the variations of this found in reports of various studies. Colors from bright yellow to green are described as characteristic for fluoride beads containing uranium. The term lemon-yellow is best suited to describe the response of the optic apparatus to the fluorescent light emitted by uranium-phosphors involving fluorides and of approximate wavelength of 5200–5800 A.U. Discrepancies of this sort are not serious but are often rather confusing.

Fluorospectroscopy

For investigational purposes the spectroscopy of the fluorescent light emitted by uranium in various bases may be useful. The utility of this is in the fact that a slight shift in wavelength of fluorescent light occurs for a change in the molecular weight of the base. Information of this type is given in the accompanying table. As is well known, phos-

phors are solid solutions, that is, uranium in sodium fluoride constitutes a solid solution. It is interesting to compare the solid solution aspect of phosphors with the solvation which occurs when solutes are dissolved in liquid solvents in ordinary solution processes. According to Feigl, every process of solution should be regarded as a chemical reaction leading to the formation of solvates, i.e., aggregations of the solute and solvent molecules.

The crests in the fluorescence spectrum of uranium in various solvents vary by several hundred Angstrom Units for the three bases listed in the accompanying table. The values in the table are nearly in inverse relation so by use of potassium phosphate with a molecular weight of 118.5 the extrapolated value of the crest should lie at about 4900 A.U. A shift in color occurs with a change in the molecular weight of the base since the color of luminescence of uranium in sodium fluoride is yellow, in calcium fluoride, sodium phosphate, and borax, green, and in potassium phosphate, blue-green. This information is based on the studies of Nichols and should be compared with the preceding comment.

FLUOROSPECTROSCOPY OF U-BEADS

<i>Solvent</i>	<i>Molecular Weight</i>	<i>Maxima (A.U.)</i>
NaF.....	42.....	5555 (Yellow)
CaF ₂	78.....	5291 (Green)
NaPO ₃	102.....	5008 (Green)

The unique and pioneering investigations of Kautsky in 1935 on the fluorescence of adsorbed molecules may have value by extended application. These concerned dyestuffs particularly, those which have been adsorbed on silica gel, but form fluorescing systems closely similar to minerals and solid solutions found in nature. A noteworthy aspect is that small amounts of adsorbed material can be subjected to flu-

orescence analysis, e.g., UO_2 , especially by the spectroscopic methods which can be used.

The procedure and apparatus is comparatively simple; a few grams of silica gel are soaked in the solution to be analyzed, e.g., dye solution, washed with water and dried. The system thus prepared is then placed in a glass vessel which can be evacuated, as well as allowing introduction of a gas. In studies on dyes a normal concentration of the dye is taken as 0.025 millimol per 10 gm. of the gel used. The vessel is irradiated by light-short ultraviolet being best suited to excite uranyl salts and inorganic materials while long wavelengths are best for excitation of dyestuffs. The criterion is in the change of intensity and nature of fluorescent light which is observed when different gases are admitted into the vessel. The molecules of silica gel do not absorb the excitational energy imparted to the molecules under study so quenching does not occur. It follows that most preparations phosphoresce for several seconds, or longer, in addition to fluorescing.

In studies on dye molecules, nitrogen, hydrogen, oxygen, carbon dioxide, and others can be used. Oxygen, of the four mentioned, very strongly quenches the fluorescence, the degree of efficiency being a function of the substance absorbed. The others have no effect on the luminescence. As would be expected the afterglow, i.e., phosphorescence is extinguished before the fluorescence. In many dyes the afterglow disappears at oxygen pressures of about 10^{-3} mm., whereas the fluorescence is quenched by pressures of about 760 mm., the considerable difference being apparent.

The difference in behavior can be ascribed to the difference in lifetime of the excited states involved and, as would be expected, longer lifetimes, i.e., phosphorescence, offer greater chance for collision with the added gas molecules, than for the shorter lifetimes, i.e., fluorescence.

After removal of the quenching gas the characteristics of the luminescent system are restored to their original state. Oxidation does not occur, quenching merely being due to transference of excitational energy from the fluorescing molecule to the oxygen molecule. As a result of this activation the oxygen can oxidize indicators, activation then being evidenced by color changes—ordinary oxygen is not capable of doing this.

Combination between uranium (solute) and solvent is probably responsible for the slight variation in fluorescence. This solvation may give rise to an intermediate complex, an aggregate or solvate, of high or low stability. If the complex is stable the fluorescence will be markedly altered; if unstable little alteration will occur. These solvates may be assumed to be the centers of emission and are formed due to electrostatic attractions.

Three types of electrostatic attraction are involved in the formation of solvates (F. Daniels, 1938). The ions, as in sodium chloride; permanent dipoles as in polar substances like water; and, induced dipoles corresponding to van der Waal's forces in neutral atoms and molecules, e.g., sodium fluoride and uranium.

Six different types of complex formation arise from interactions between these three different forms of attraction. When the solvent is involved as one unit the mechanism is solvation. If the components of the solvent, i.e., ions, are involved chemical combination results. These are not sharply distinguished and may overlap. The strength of the bonds, it follows, are in inverse relationship to the dielectric constant of the solvent.

The relationship which solvates have to the dielectric constant of their medium is illustrated in the equation:

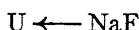
$$\epsilon = \frac{2\mu_A\mu_B}{D r_0^3}$$

In this ϵ is the energy which binds the two molecules, e.g., U and solvent together in a head-on position and μ_A , μ_B , D , and r_0 are the dipole moments of the substances A and B, the dielectric constant of the medium, and the shortest distance between the two molecules, respectively.

A related but somewhat different aspect of solvation is in the explanation of E. S. Hedges (1932); being applicable also to uranium phosphors and the formation of aggregates. In this explanation solvation of the ions is considered separately since ions exist in the lattice of the salt. Each ion is coordinated with its solvent molecules with coordination occurring in two ways. In one, the solvent acts as the acceptor:



or, by the solvent acting as the donor:



Which action occurs depends, of course, upon the nature of the solvent. The formation of a semipolar link tends to give a positive charge to the donor and as a result the atom is more likely to become a donor when it is negatively charged so that anions will be donors and cations (uranium as U^{4+} or UO_2^{++}) acceptors:



It seems unfortunate that the knowledge concerning solid solutions and the nature of alloys, and other entities of this sort, has not been applied more to phosphors where striking applications are forthcoming.

From the foregoing evidence it would appear that the actions which lead to the formation of solvates or clusters of solute and solvent molecules in liquid solutions also occur in solid solutions. The application of the formation of solvates in solid solutions is to phosphors for the explana-

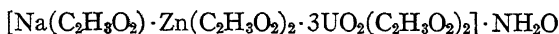
tion of variance in fluorescence wavelengths of uranium in different solvents.

Organo-uranium phosphors, viz., those which involve an organic base were mentioned as being not studied extensively. In this type of phosphor the activator, e.g., uranium, may be incorporated into the lattices of the base at relatively low temperatures, e.g., 60° C. The use of certain glyceryl ethers, stearates, and others which have a low melting point, and which have been previously shown to be suitable in such a preparation, is indicated when the activating entity is decomposed, viz., uranyl acetate, or altered by the temperatures used in the production of the ordinary type of phosphor. Temperatures used in the production of sodium fluoride phosphors (beads), for example, are as high as 900° C. Thermal changes as great as this cannot be encountered in many investigations without alteration being produced in the specimen.

It is noteworthy that uranyl acetate is much more soluble in glyceryl alpha monophenyl ether than in glyceryl alpha gamma diphenyl ether.

Microchemical Methods

Microchemical detection of uranium is usually performed by sodium acetate and zinc acetate, these reagents forming:



The test solution is prepared by mixing dilute acetic acid, sodium acetate, and zinc acetate. These are placed on a slide and evaporated to dryness so that a thin even film is produced. The solution containing the material to be tested is placed in a drop nearby and acidified with acetic acid.

The drop is drawn in a narrow streak across the dried film. A positive reaction is denoted by tetrahedra of sodium uranyl

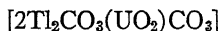
acetate. These may also be octahedra-like monoclinic, polysynthetic twins of sodium zinc uranyl acetate.

Other elements which may form double uranyl acetates are K, Rb, Cs, Tl, NH_4 , and Ag:



These salts separate into long slender needles, or may be in the form of slender tetragonal prisms, which terminate in pyramids. These constitute an isomorphous series and are more soluble than the sodium salt. Therefore, they do not separate as readily from solution. The reaction is peculiar to uranium alone and is subject to sources of error due to the formation of uranium as an insoluble salt (Chamot and Mason, 1931).

According to H. Behrens the double salt test using thallium sulfate is more sensitive than the previous test. In this thallium sulfate is added to a solution containing ammonium carbonate, these forming with uranyl ions:



The test is rather difficult to obtain except when comparatively pure uranium compounds are used or else when performed under carefully controlled conditions.

The procedure is as follows. To the specimen ammonium hydroxide is added in order to precipitate the uranium as the uranate. The precipitate is separated by micro-filtration or centrifugation. The uranate is then dissolved in ammonium carbonate solution and a fragment of thallium sulfate or nitrate added. A layer of double salt crystals form about the fragment in a few minutes. The crystals also grow away from the fragment.

The crystals are probably orthorhombic and take the form of rhombic plates which are of varying irregularity in addition to 3, 4, and 6 sided tabular crystals or grains.

The test should always be confirmed by decantation of the mother liquor and the precipitate flooded with a solution of potassium ferrocyanide in acetic acid. A brown coloration indicates the presence of uranium. This should make the test conclusive provided copper has been proved absent.

One part of uranium in 5000 may be detected by means of the thallous uranyl tricarboxylate microchemical test. Although this does not measure up to certain other methods it presents many advantages when used by an experienced microchemist. The procedure in this test is essentially the same as the foregoing test.

Another microchemical test for uranium is by use of oxalic acid. With this reagent or with oxalates the separation of hydrated uranyl oxalate occurs in the form of very pale yellow orthorhombic prisms and plates, the latter of which are thin, rectangular, or square.

Fluorescence Analysis

*Fluorescent Light And Its Applications** describes the luminescence of radioactive minerals (uraniferous minerals) rather completely. The reader is referred to this work.

The radioactive minerals seem to be of universal interest with their relation to fluorescence. The rather widespread fallacy that all radium bearing minerals are highly fluorescent is perhaps one of the causes of this interest. This is in spite of the fact that a few, but not all of the radium bearing minerals are fluorescent.

In the instances of fluorescent radioactive minerals evidence fails to show that the phenomenon is directly attributed to the radium present in the specimen. Instead, the fluorescence is directly related to the uranium present and the type of salt in which it exists. Fluorescence, on a macro-

* Dake and De Ment, *Fluorescent Light and Its Applications*, Chemical Publishing Company, Brooklyn, New York.

scopic scale at least, has provided a valuable adjunct for qualitative tests as to the uraniferous nature of minerals. As has been pointed out previously the presence of uranium in a mineral invariably presupposes the presence of radium.

Primary uraninites are non-fluorescent. A large number of secondary uraninites are highly fluorescent. Since outcroppings of pitchblende (see the chapter on prospecting) are, in many instances, coated with secondary minerals produced by alteration (weathering) prospecting with ultra-violet radiation is often valuable. It should be emphasized, however, that the lack of fluorescence does not indicate the absence of uranium, e.g., uraninite or carnotite.

For methods of study of mineral specimens the reader is again referred to the writers' previous work which treats all phases of fluorescence analysis extensively. In the same work the action of uranium as an activator is described.

The difficulty encountered in differentiating the rare secondary radioactive minerals is well known. A qualitative spot test has been used to roughly distinguish between specimens appearing the same under ultraviolet radiation. For example, autunite and schroeckingerite often appear about the same. By spotting the surface of the specimens with chemical reagents, e.g., HCl, HF, HNO₃, H₂SO₄, H₂SO₄-NaF, NaOH, or others alterations in fluorescence color are produced because of the different products developed from the reaction. These differences enable discrimination of two specimens that cannot be otherwise subjected to the usual analytical means.

Spot tests may also be performed with fragments several millimeters in diameter as well as on the surface of large specimens. A set of standard reagents and a series of known radioactive minerals makes it possible at times to identify a species. The test appears to be useful since data on the properties of radioactive minerals is often scant and of a varying

nature. The final consideration in use of this test consists of strict standardization of working conditions and discretion in application.

Intermittent investigations have been performed on the X-ray fluorescence of uraniferous minerals. Studies by the present writers, et al (1940) showed that the majority of the secondary uraninites fluoresced whereas primary minerals do not. Several varieties of secondary minerals phosphoresced strongly after X-ray excitation although the same specimens do not ordinarily phosphoresce with ultraviolet radiation as the exciting agent.

Uranium-containing agate from Sweetwater County, Wyoming fluoresces a yellowish-green color with no differences being noted between the specimens with visible inclusions of ferghanite (?) and those without the inclusions, i.e., translucent agate. A strong phosphorescence of several seconds duration is noted in these agates after exposure to the X-rays.

URANIFEROUS MINERALS UNDER X-RAYS

(83 Kv./20 ma., 0.5 mm. Al)

<i>Mineral</i>	<i>Fluorescence</i>	<i>Phosphorescence</i>
Autunite.....	Yellowish.....	Dull green
Carnotite.....	None.....	None
Pitchblende.....	None.....	None
Gummite.....	None.....	None
Schroëckingerite.....	Yellow-green.....	None
Meta-torbernite.....	Yellow-blue.....	None
Uraniferous Agate.....	Yellow-green.....	Dull whitish-green
Uraniferous Opal.....	Yellow-green.....	Dull whitish-green

A general summary of the fluorescence characteristics of uranium minerals would include:

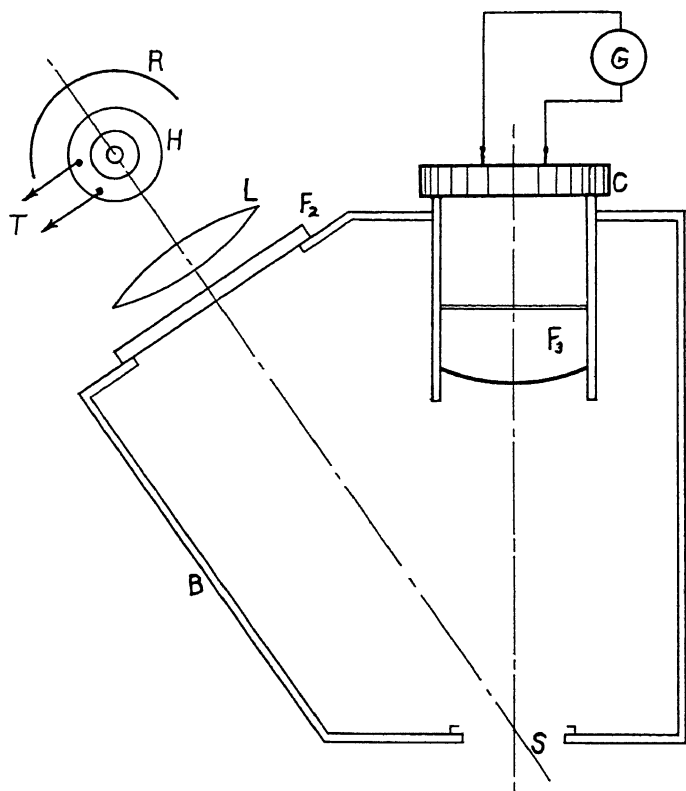
- (1) Primary uraninites do not fluoresce.
- (2) A number of secondary uranium-containing minerals are highly fluorescent, i.e., those which contain the uranyl group.
- (3) In practically every case of fluorescence the characteristic uranium yellow-green color is observed.
- (4) Generally, more soluble uraniferous minerals are usually those which are more fluorescent.
- (5) The largest number of fluorescent uranium minerals are those which have a specific gravity of about 3.5. Few uraniferous minerals with a high specific gravity (e.g., 9.5) are fluorescent.
- (6) Fluorescence is best excited by short wavelength ultraviolet radiation of high intensity (i.e., wavelengths of 2537 A.U.—mercury resonance radiation).
- (7) Primary uraninites after weathering frequently alter to secondary and fluorescent species. In this way a dual detection may often be made.
- (8) The presence of uranium invariably presupposes the presence of radium.

Fluorophotometry and Solution Operations

The fluorophotometer is effective for the detection and determination of gamma-sized quantities of uranium in solution. With it two analytical approaches may be used. In one, the direct measurement of uranium by its fluorescence is successful in rather pure solutions, provided the uranium exists as the fluorescent UO_2 entity and is not attached to quenching anions. In the other, the measurement of fluorescence is accomplished by addition of certain metal ions, or others (e.g., silver) which produce, in very small amounts, a quenching effect. The fluorophotometer is one of the most precise devices known for the determination of small amounts of material without alteration being required, in many in-

stances, for analysis. Destruction of the specimen is typical of most other analytical methods.

The direct vision fluorometer, or fluorophotometer, of F. E. E. Germann and J. W. Hensley of the University of Colorado is typical of a number of instruments which allow the precise quantitative determination of the intensity of fluorescence. The direct vision fluorometer is shown in the



The Germann and Hensley Direct Vision Fluorometer. With this instrument very precise studies on the quantitative aspects of fluorescence may be made. Currents of less than 3×10^{-11} amps. can be estimated with devices of this sort (modified by L. Zill). See text for description.

accompanying diagram. The source of ultraviolet light is a capillary mercury vapor lamp, reflector and transformer (H, R, and T). The ray is focussed by a quartz lens (L) and filtered by a CG 986 filter (F_2), two of which may be used (F_1 not shown). The specimen is placed at S and the sodium nitrite cell (F_3) prevents ultraviolet light from affecting the selenium cell (C), connected to a sensitive galvanometer (G). The results are expressed statistically; graphs being the ordinary and convenient means of notation.

Exceedingly small amounts of certain substances will quench the fluorescence of uranium solutions. A test which may be used indirectly to indicate the presence of uranyl nitrate is that of Volmar and Mathis (1934). In this test a reagent consisting of uranyl nitrate and sulfuric acid is added to the substance to be examined. Pure pharmaceutical materials will not affect the fluorescence of this uranyl ion containing reagent whereas pharmaceutical materials which contain impurities in the slightest amount will quench or extinguish the fluorescence.

In 1940 H. Goto conducted investigations on the detection of a number of ions by their fluorescence. These studies included uranium. This investigator found that one gamma of silver will prevent the fluorescence of uranyl sulfate solutions.

This may be used indirectly to detect the presence of uranyl ions, the addition of reagent being made to a known silver solution. Thallium, in the lower valence state, acts like silver in this respect. The white precipitate formed on adding arsenate solutions to the uranyl compounds produces a yellow-green fluorescence with as little as 0.5 gamma of arsenic. An indirect test for uranium is suggested here again. The arsenite ion behaves similarly. The use of the fluorophotometer for measuring the intensity variations on addition of these ions to uranyl ion solutions is indicated.

Fluorescence methods for the detection of sodium by use of zinc uranyl sodium triple acetate (see section on microchemical methods) are sensitive to 0.5 gamma. Goto found that one gamma of lithium produces a yellow-green fluorescence in the formation of the triple acetate like the previous salt except that lithium takes the place of the sodium. Spectrograms were prepared by Goto for uranium, analysis being made from the sodium fluoride bead test which was found to be sensitive to 0.02 gamma of uranium.

The quenching effect of various ions is shown in the following table. Other substances which may be useful in a quenching-type test are also given. It is noteworthy that in low concentrations of the following salts of the alkali metals the intensity of the fluorescence is a decreasing exponential function of the concentration of uranium.

QUENCHING EFFECT ON URANIUM

After Perrin

<i>Quenchers</i>	<i>Non-Quenchers</i>
S ⁺⁺	NO ₃ ⁻
SCN ⁻	Cl ⁻
I ⁻	* Br ⁻
NO ₂ ⁻	F ⁻
S ₂ O ₃ ⁼⁼	CN ⁻
S ₂ O ₄ ⁼⁼	CO ₃ ⁼⁼
HAsO ₃ ⁼⁼	SO ₄ ⁼⁼
Alkaloids	Urea
Aniline	Sugars
Tannin	Alcohols
Phenol	Pyridine
Cresol	Acetamide **

* Compare this with data on the fluorescent peracid reaction in a following section.

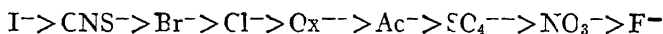
** Compare this with fluorescence tests described in the section on amine precipitants.



Conti-Glo "black light" of the spot-light type, with parabolic reflector and convex filter. Well suited for the examination of secondary uranium minerals and uranium compounds for fluorescence. (Photo: Continental Lithograph Co., Cleveland, Ohio)

Parabanic acid, sodium cyanide, and sodium cyanate, act as non-quenchers for the fluorescence of the uranyl ion also.

The quenching of the uranyl ion is a function of the deformability of the added quenching solution (after the experimental results of West, Muller, and Jette in 1928). The fluorescence inhibiting effect of various ions varies slightly for different substances but the following general order of quenching efficiency holds with the uranyl ion:



It is interesting to compare this information with the information of F. Perrin in the accompanying table.

On the other hand, fluorescence enhancing anions may be useful in analysis. In the following table some of these ions are listed. The inorgano-uranium anions have been chosen mainly on the basis of their occurrence in nature in fluorescent substances, i.e., secondary uraniferous minerals.

FLUORESCENCE ENHANCING ANIONS IN URANYL ENTITIES

Inorgano-uranyl *

Arsenate
Phosphate
Carbonate
Sulfate
Vanadate

Organo-uranyl **

Hydroxyl
Methoxy
Methylene
Amino
Nitrile

* Based on data from *Fluorescent Light and Its Applications*, by Dake and De Ment, Chemical Publishing Company, 1941.

** Based on data from *Phosphorescenz*, by R. Tomaschek, Leipzig, 1927.

In the accompanying table quenchers are given which are primarily of an organic nature. These, contrasted to the ions, electrolytes, and similar materials emphasized more in the studies by Perrin, and others, are of a widely varying nature.

ORGANIC URANIUM QUENCHERS

Mesityl oxide	Tannic acid
Glyceryl alpha-mono chlorohydrin	Cresol
Butyl borate	Calcium pantothenate
Xanthone	Inositol
Butyryl pyrogallate	dl-Methionine
	Sodium nucleate

Of especial value in study of small amounts of uranium may be the factor of depolarization of light diffracted by liquids. The basis for this form of analysis for small quantities of substances is based on the investigations of A. Bourtari in 1934. The factor of depolarization of light scattered by liquids is related to anisotropy.

The factor of depolarization allows determination of anisotropy and decreases with the number of double bonds in a molecule, e.g., organo-uranium compounds. The factor is increased when alkyl groups are introduced into cyclic hydrocarbons. It may be used for determination of purity or for the detection of slight traces of fluorescence. In the estimation of traces of fluorescence the factor is measured both with and without the radiation exciting the fluorescence and the amount is obtained from the relationship between the two factors.

The depolarization factor is defined as:

$$\rho = \frac{I_w}{I_s}$$

where I_s is the intensity of the component polarized and passing through the plane about the line of sight at a maximum whereas I_w is the intensity of the component polarized and passing through the plane at a minimum. The depolarization is:

$$\Delta = 2I_w(I_w + I_s) \equiv 2\rho/(1 + \rho)$$

In studies on uranyl salts discrimination between closely related salts may be obtained by fluorescence analysis. The special procedure used is based on activation with water. Hydrated and dehydrated salts, immediately after preparation, are examined in long wavelength ultraviolet radiation (if organic) and/or in short wavelength ultraviolet radiation (if inorganic). The method is used more effectively on organo-uranium salts.

WET-DRY FLUORESCENCE OF URANYL SALTS

(E) $\lambda = 3650 \text{ A.U.}^*$

<i>Uranyl</i>	<i>Wet-phase</i>	<i>Dry-phase</i>
Tungstate.....	Bluish.....	Purplish
Molybdate.....	Bluish.....	Violet
Stannite.....	Pale blue.....	Pale blue
Ferrocyanide.....	Deep red.....	Lavender
Nitrite.....	White (violet).....	White (violet)
Monphosphate.....	Strong blue-green.....	Strong blue-green
Fluoride.....	Pale blue.....	Pale blue
Thiocyanate.....	Pale blue.....	Pale blue
Tellurite.....	Pale scarlet.....	Pale scarlet
Tetraborate.....	Blue.....	Violet
Aluminate.....	Strong blue.....	Strong blue
Amytal.....	Strong blue.....	Strong blue
Chromate.....	Red.....	Crimson
Salicylate.....	Red.....	Crimson
Iodide.....	Red.....	Pink
Citrate.....	Reddish.....	Pink
Bicarbonate.....	Strong blue.....	Lavender
Gluconate.....	Pale blue.....	Blue
Oxychloride.....	Pale blue.....	Pale blue
Chromate.....	Red.....	Crimson

* It will be noted that long wavelengths such as the (E) λ used here are directed more towards fluorescent properties of the anion with which the uranyl group is associated. Short wavelength radiation (e.g., Hg resonance radiation as (E) $\lambda = 2537 \text{ A.U.}$) would cause the UO_2 to fluoresce and thus mask fluorescence in the anion. Here the UO_2X entity is fluorescing and not the UO_2 singularly.

This method has been used with satisfactory results on rare earths which are closely related. Examination in both wet and dry phases indicates that differentiation is possible since variations are much more apparent under these conditions. A series of uranyl salts in long wavelength ultraviolet radiation (3650 A.U.) in both phases is shown in the table on page 250.

Fluorescence analysis can be considered unique among most methods of chemical investigation. Oftentimes fluorescence makes it possible, by relatively simple techniques, to deal with problems and phenomena on the threshold of measurement, perhaps a dangerous region for investigation.

The following resume lists some of the more important and accessible factors and conditions, together with their literature references, which pertain to the fluorescence of uranium and to the various effects which may be of utility for special investigation and procedure.

FACTORS PERTINENT TO URANIUM STUDIES BY FLUORESCENCE

<i>Condition or Factor</i>	<i>Reference</i>
Quenching by electrolytes. . . .	Radley and Grant, <i>Fluorescence Analysis in Ultra-Violet Light</i> , p. 198, New York (1939), 3 ed.
Excitation proportional to wavelength of exciting agent and independent of concentration at high dilutions. . . .	Ghosh and Sen-Gupta, <i>Z. phys. Chem.</i> , B41 , 117 (1938).
Changes due to addition of cations	Goto, <i>J. Chem. Soc. Japan</i> , 59 , 547 (1938).
Hydrocarbons of high molecular weight, or with unsatu-	

FACTORS PERTINENT TO URANIUM STUDIES BY FLUORESCENCE—(*Continued*)

<i>Condition or Factor</i>	<i>Reference</i>
rated conjugated double bonds most effective for quenching	J. Eisenbrand, <i>Z. phys. Chem.</i> , B22 , 145 (1935).
Quenching by halogens increases with atomic weight..	Volmar and Mathis, <i>Bull. Soc. Chim.</i> , 53 , 385 (1933).
Quantitative exponential expression derived for intensity in terms of the concentration.	J. Bouchard, et al, <i>Compt. rend.</i> , 196 , 485 (1933).
Quenching by compounds of an anti-oxygenic nature (see text)	F. Perrin, <i>Compt. rend.</i> , 186 , 428 (1928).
Quenching a function of the deformability of the anion added	West, et al, <i>Proc. Roy. Soc.</i> , A121 , 294 (1928).
Determinations at high dilution.	Hernegger and Karlik, <i>Sitzungsber. Akad. Wiss. Wien</i> , 144 , 217 (1934).
Effects of supercooling to -180° C.	Nichols and Howes, <i>Carnegie Inst. Wash. Pub. No.</i> 298 (1919).
Activating action in solid solution (see text on bead tests).	Nichols, et al, <i>Carnegie Inst. Wash. Pub. No.</i> 384 (1928).
Purity of the salt or solution...	Present writers, see text.
Stability of U systems under intense irradiation by ultra-violet light.....	Roy, <i>J. Indian Chem. Soc.</i> , 6 , 431 (1929).

FACTORS PERTINENT TO URANIUM STUDIES
BY FLUORESCENCE—(*Continued*)

<i>Condition or Factor</i>	<i>Reference</i>
Correlation of Solubility and fluorescence of natural compounds	Dake and De Ment, <i>Fluorescent Light And Its Applications</i> , p. 142, New York (1941).
Enhancing anions from and in naturally occurring compounds	See text.
Fluorescence a function of the valency, with U being the exception	Haitinger, et al, <i>Mikrochemie</i> , 10, 117 (1930).
Dispersion in suitable substrates to enhance fluorescence	Haitinger, <i>Die Fluorescenz-analyse</i> , p. 24, Vienna (1937).
Dessication effects	Present writers, see text.
Depolarization factor (see text)	N. E. Dorsey, <i>Properties of Ordinary Water Substance</i> , p. 300, New York (1940).
Salting-out	A. Banov, <i>Z. phys. Chem.</i> , A163, 172 (1932).
Dipole moment and degree of dissociation of solvents	J. Eisenbrand, <i>Z. f. phys. Chem.</i> , B 22, 145 (1933).
Duration of Emission with the nature of the exciting agent. .	E. Hirschlaff, <i>Fluorescence and Phosphorescence</i> , p. 123, New York (1939).

Exciting Agents

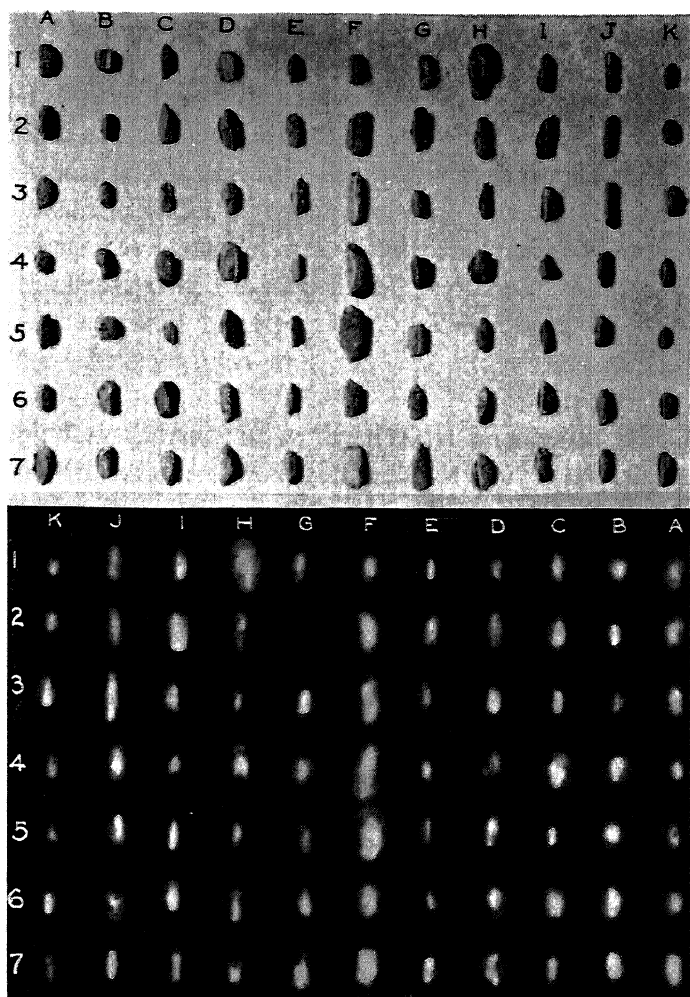
The influence of the nature of the exciting agent upon the type and duration of fluorescence is well known. Although

uranium compounds are best excited by ultraviolet radiation of wavelength 2537 A.U., and thereabouts, other agents may determine the variation which may occur in the luminescence of uranium salts. Photo-excitation of centers having different lives has been demonstrated. It has been found that electrons, e.g., beta rays, usually excite centers with a short life, although this is by no means a general law. Uranyl sulfate crystals, for instance, have an emission lasting for 0.003 sec. when excited by light; X-rays produce an afterglow of some seconds, and this afterglow is extended to several minutes when excited by cathode rays.

Further, exciting agents can destroy the phosphor in some cases. Although alpha rays may eventually cause destruction of the phosphor, but not necessarily pure compounds which are fluorescent, i.e., uranyl salts, and probably not their solutions. Alpha rays, however, are not used extensively as exciting agents. X-rays and gamma radiation, on the other hand, do not much affect phosphors. Alpha rays, X-rays, and gamma radiation are not used for the excitation of solutions in routine analysis but may be of use in research, especially on minerals and phosphors, or solid entities which involve uranium.

Radiographic Tests

The photographic method for detecting uranium has been used extensively. In this test the specimen is usually placed directly on an unexposed photographic plate although the preferable procedure is to separate the specimen and plate by several thicknesses of paper. After exposure, which may range from several hours to several weeks, the plate is developed and inspected. The general opinion in most cases is that exposure indicates the presence of uranium and radium. Unfortunately, from an analytical standpoint this is not always true, since other radioelements are known and these affect the plate also.



Water worn fragments of uranium-bearing minerals from the gold placer mine of Carlos Poncia, Centerville, Idaho. Note tendency to prismatic form. Radiograph (below) of 48 hours exposure. The radiograph shows that although fairly even in composition, some specimens are richer in uranium, or thorium, or both. (Photo: Frank L. Hess, U. S. Bureau of Mines).

Although the test is advantageous in the respect of being sensitive in approximate proportion to the time of exposure it is not reliable. Novices frequently make the mistake of placing the specimen directly on the plate. When this is done photographic effects are caused by pressure and may be confused with true exposure of the plate. In 1909 Ebler pointed out that "pseudoradioactivity" may simulate radioactivity in that some substances affect a plate which are themselves void of any true radiation emitting power. This method is unreliable and its use has not been recommended (S. C. Lind, 1923).

On the other hand, in the hands of an expert the technique is a valuable adjunct to other modes of detection. Its value for preliminary and large scale tests is well known to those who have used it. The test is of import for research purposes. It should be emphasized that thorium elements may affect the emulsion and such effects may be confused with those due to radium and uranium. A typical radiograph of radioactive minerals is shown in the accompanying illustration, this having been prepared by an expert analyst.

In radiographs of radioactive minerals two effects will be noted. If a rough specimen is exposed to the photographic plate, portions of the developed plate will be out of focus, due to the varying distances between specimen and the photographic plate. If the rough specimen is sectioned and the smooth flat surface exposed to the plate, all areas containing radioactive material will appear in focus.

Spectrochemical Methods

At present the spectrochemical method for the detection or determination of uranium is far from satisfactory. The primary reason for this is rather apparent. The extremely complex nature of the uranium atom itself is the determining

factor in the complexity of its spectrum. As a result of the little or no characteristic information that is yielded from spectrograms obtained from ores low in uranium content the practicability of the method suffers considerably.

It has been pointed out that concentrations of 7% or less of uranium do not respond satisfactorily to spectroscopic analysis. In antithesis, spectrochemical technique has and will continue to provide numerous valuable approaches to newer knowledge about uranium, the use of the spectroscope for research purposes still remaining important.

A thought-provoking test is that of *reflection spectrometry* originated by G. Urbain in about 1900 and used by Kithil in 1916. The test is intended primarily for monazite but may have value in uranium mineral studies since these often have a characteristic color (cf. the reflected visible uranium-yellow light with that of the similar yellow fluorescent light). In this technique the determination is made by inspecting plane layers of sand or powder with a hand spectroscope held at a convenient angle so that the natural light falls directly on the specimen.

For monazite a fairly dark broad band will appear between the red and yellow regions of the spectrum while another band will be observed in the green region of the spectrum. These dark absorption bands seem to be due primarily to the presence of rare-earths such as the oxides of neodymium, praseodymium, and erbium which are present in this mineral. It is stated that such tests are fairly reliable and accurate if used by an experienced observer.

The entire spectrum is divided into a scale 63 mm., the first and broader dark lines becoming visible between the 13 and 15 mm. lines. The narrow dark lines appear between 21 and 22 mm. on the scale.

This method of spectroscopy, while not well known, is useful for the field and is suggested as being most helpful in

far-away places where a laboratory is not available. The method will also serve in the laboratory for purposes of preliminary examination or for rapid check tests.

PRINCIPLE LINES IN THE EMISSION SPECTRUM OF URANIUM

After J. A. Hannum

397	4394	5669	7425
764	4472	5724	7534
1587	4544	5758	7619
1833	4627	5781	7632
1981	4647	5799	7784
1985	4689	5838	7882
2008	4732	5915	7970
3567	4757	5976	8223
3670	4773	5997	8262
3831	4819	6052	8318
3860	4899	6077	8382
3832	5027	6172	8445
3986	5280	6372	8450
4090	5476	6395	8496
4157	5481	6449	8505
4164	5493	6465	8540
4172	5528	6827	8608
4242	5564	7075	8686
4289	5611	7102	8691
4342	5622	7129	

Microspectroscopy

In regard to spectroscopy of uranium solutions where absorption bands are often determining criteria a somewhat different importance is noted. Absorption spectroscopy has a number of advantages over emission and related forms of analysis. This is mainly due to the relative simplicity of the spectra as compared to the thousands of fine lines in other types of spectra for uranium. The absorption spectra, i.e.,

main absorption bands, of a number of uranyl salts were determined by Morton and Bolton in 1873. The studies of these investigators included two series of double salts, the acetates and the sulfates. The accompanying table lists the absorption bands of several of these salts.

Absorption bands assume added importance when it is realized that the facts presented here can be applied to *microspectroscopy*. The essence of this is absorption spectroscopy of specimens such as single minute crystals on the stage of a microspectroscope. The microspectroscope, or spectromicroscope, consists mainly of a microscope containing an auxiliary diffraction grating on the ocular or other form of direct vision spectroscopy to be used in conjunction with microscopic inspection of the specimen on the stage.

ABSORPTION BANDS OF DOUBLE URANYL SALTS

After Morton and Bolton

<i>Uranyl Salt</i>	$\lambda = \text{Angstrom Units}$				
Ammonium uranyl acetate...	4620...	4455...	4310...	4200...	4075
Barium uranyl acetate.....	4625...	4465...	4330...	4200...	4075
Cobalt uranyl acetate.....	4625...	4465...	4335...	4200...	4080
Potassium uranyl acetate...	4625...	4460...	4320...	4200...	4070
Lithium uranyl acetate.....	4620...	4455...	4320...	4205...	4080
Magnesium uranyl acetate...	4627...	4480...	4337...	4215...	4085
Sodium uranyl acetate.....	4620...	4453...	4310...	4185...	4055
Rubidium uranyl acetate...	4625...	4465...	4315...	4202...	4080
Strontium uranyl acetate...	4627...	4480...	4335...	4205...	4075
Thallium uranyl acetate...	4640...	4480...	4320...	4205...	4085
Zinc uranyl acetate.....	4655...	4490...	4340...	4325...	4100
Ammonium uranyl sulfate...	4935...	4800...	4620...	4450...	4330
Ammonium diuranyl sulfate...	4875...	4720...	4575...	4480...	4330
Magnesium uranyl sulfate...	—	4790...	4540...	4370...	4230
Potassium uranyl sulfate...	—	4790...	4540...	4370...	4230
Rubidium uranyl sulfate...	4885...	4805...	4645...	4475...	4325
Thallium uranyl sulfate.....	4905...	4630...	4480...	4295...	—
Sodium uranyl sulfate.....	4875...	4775...	4580...	4440...	4335

Amines as Precipitants

The use of ammonium hydroxide to precipitate uranium from solutions in the form of yellow insoluble uranates has been discussed previously. Other tests exist which are related to this type of reaction. Moreover, other amines may be used instead of ammonium hydroxide, these probably precipitating or reacting with uranium to form uranates or poly-uranates.

Monomethylamine was used by F. de Coninck as such a reagent. The uranium was precipitated from sulfuric acid solution in the form of a dark brown precipitate, this being soluble in dilute acids. Another amine, ethylenediamine in 10% solution, precipitates uranium in a bright yellow colored form. This precipitate is insoluble in organic solvents and no other elements are precipitated under the same conditions (Siemssen, 1911).

Alkaline solutions of thiosinamine precipitate uranium in a bright yellow form and according to Lemaire (1909) no other alkaline earth or heavy metal except cadmium yields a precipitate with this reagent.

Another amine, pyridine, is mentioned frequently in the literature as being of use in the analysis of uranium.

Ray's test (1931) is another in the amine category. In this members of the "ammonium group," consisting of iron(ic), aluminum, uranium (as uranyl), titanium, and zirconium are precipitated at boiling temperature by the addition of a 10% solution of hexamethylenetetramine to a neutral solution of the above elements in the presence of ammonium chloride.

Studies by the present writers on a number of amines not noted in other studies are shown in the accompanying table. There is reason to believe that many amines exist, other than those mentioned by previous investigators, which may be

useful in quantitative precipitation of uranium. In practically all of the amine tests for uranium a yellow precipitate or color is formed. The three amines, monomethylamine, dimethylamine, and trimethylamine reacted in the same general way as did dibutylamine and isopropylamine.

AMINES AS URANIUM PRECIPITANTS

For UO_2^{++}

<i>Amine</i>	<i>Color and Nature of Precipitation</i>	<i>Fluorescence (2537 A.U.)</i>
Monomethylamine.....	Yellow-white.....	Rose
Dimethylamine.....	Yellow-white.....	Rose
Trimethylamine.....	Yellow-white.....	Rose
Dibutylamine.....	Bright yellow.....	Deep rose
Isopropylamine.....	Bright yellow.....	Deep rose
2-amino-1-butanol.....	Clear yellow solution.....	Red-brown
2-amino-2-methyl- 1-propanol.....	Clear yellow solution.....	Red-brown
2-amino-2-ethyl- 1,3-propanediol.....	Voluminous yellow flocculant precipitate..	Rose
Tris (hydroxyamino) methane.....	Voluminous yellow flocculant precipitate..	Rose
2-amino-2-methyl- 1,3-propanediol.....	Voluminous yellow flocculant precipitate..	Rose
Hydroxylammonium sulfate.....	Pale yellow solution.....	Pink
Pyridoxine hydrochloride.....	Bright yellow.....	
Pyridine-beta-carboxylic acid diethylamide.....	Bright yellow solution.....	Rose
Diphenylamine.....	Nil.....	—
Allylamine picrate.....	Nil.....	—
Aminoacetal picrate.....	Nil.....	—
Ethanolamine hydrochloride..	Nil.....	—

Amines of a more complex nature produce interesting results when allowed to react with uranyl salt solutions. Three higher amines of probable importance as uranium precipitants are 2-amino-2-ethyl-1,3-propanediol; tris (hydroxyamino) methane; and, 2-amino-2-methyl-1,3-propanediol. With solutions containing a fraction of a milligram of uranium per cubic centimeter bright yellow precipitates may be obtained. At greater dilutions a yellow color is noted. In 2-amino-2-ethyl-1,3-propanediol solutions with as little as 0.05 mg. of uranium a very slight, but visible, yellow coloration is produced.

Other aspects of the investigation may be interesting. Three reagents were prepared which made it possible to detect uranium in amounts as low as 0.1 mg. per cc. by the yellow coloration formed when added to uranyl salt solutions. The interference of other elements was not ascertained but it is quite probable that interference does exist, the extent of which was not revealed by the study. The reagents used appear to be superior, as a series, to the test of Hackl and others. They may be used in qualitative confirmatory tests or after amplification in detail may be useful for actual quantitative determination of uranium.

In one, hydrogen peroxide is saturated with 2-amino-2-ethyl-1,3-propanediol and used while cold. A clear bright yellow coloration is formed on addition to comparatively pure solutions of uranyl salts. The second reagent consists of a hydrogen peroxide solution of both tris (hydroxyamino) methane and 2-amino-2-methyl-1,3-propanediol, a clear bright yellow coloration also being formed with uranyl ions. Apparently more sensitive is a hydrogen peroxide saturated solution of 2-amino-2-methyl-1,3-propanediol; tris (hydroxyamino) methane; and, 2-amino-2-ethyl-1,3-propanediol. The reagent itself has a slight yellowish tinge but

when very small quantities of uranyl salts are added the depth of the yellow color is increased markedly.

Higher amines were also studied to a small extent (see table). The results indicated that more complex amines do not appear to be of much value in tests of this sort. In two amine picrates tested, allylamine picrate and aminoacetal picrate, any color due to uranium was masked by the original yellow color of the reagent. Diphenylamine did not react nor did ethanolamine hydrochloride. The precipitates and solutions in all tests were inspected under short wavelength ultraviolet radiation.

A clear bright yellow solution is formed when uranyl salts are added to furfuryl reagents. A sensitive test of this sort consists of tetrahydrofurfuryl alcohol saturated at room temperature with hydrofuranide. Another reagent with greater limits of detection is that in which tetrahydrofurfuryl alcohol is saturated with trifuryldihydroimidazole (furfurin), a salt which is the isomer of hydrofuranide. Furfurin is more basic than hydrofuranide and forms well defined salts with acids. Uranyl salts also produce a bright yellow color with this reagent.

Theophylline-diethylenediamine in methanol solution form a yellow coloration with uranyl ions. Methanol solution of both p-phenylenediamine and o-phenylenediamine react with uranyl salt solutions in an exceedingly interesting manner. When either of these are added to uranyl ions a yellow solution is formed which rapidly changes to a dirty green colored precipitate. Often a dirty green-brown color is obtained in the course of this reaction. An alcoholic solution of p-acetylaminophenol reacts with uranyl salts in neutral solution to form a clear light brown-colored solution.

From the foregoing evidence it would appear that uranyl ions are associated with some special activity or binding ac-

tion which is possessed by/in many amines. It is apparent that the uranate reaction does not adequately explain all those reactions which involve higher amines and uranyl ions. Special binding of certain other metal ions often occurs and special binding of the uranyl ion may exist.

Illustrations of specific activity have been given by Feigl (1940). For example, the nickel binding group is $-C(NO_2H)$; the copper specific groups are $-C(OH):C(NO_2H)$ and $-C_6H_4(OH)C(NO_2H)$; the silver binding group is NH ; the thallium specific group is $-CO-CH_2-CO-$; the zirconium binding group is $-As(OH)_2$; the $-O-OH$ group exerts special action on peracids (uranium, as well as Mo, Ti, and others, is included in this extremely delicate test); hydroxyanthraquinones behave in somewhat predictable ways, e.g., the 1,2-dihydroxy salt forms a lake with uranium; and, many others for iron, and other elements, are known.

The *imide group* may be the explanation of the special binding or selective activity possessed by amines for uranyl ions.

Microscopic Determination

Investigations on the microscopic methods for determination of uranium minerals are not extensive. Short (1940) treated uraninite as being isometric, dark gray in color, and of hardness in the ilmenite class. Nitric acid stains uraninite differentially brown while hydrochloric acid and potassium cyanide solution produce no reaction. Ferric chloride solution slowly tarnishes the mineral to a still darker brownish-gray. No reaction is obtained with potassium hydroxide and mercuric chloride solution. The substance is massive and the powder is greenish-brown to black. The information of Short compares favorably with practically all other data obtained by different modes of study.

Davy and Farnham (1920) also listed uraninite in their determinative tables for microscopic examination of opaque minerals. Their data indicates that uraninite is negative to nitric acid and potassium cyanide, while ferric chloride slowly tarnishes the specimen to a still darker brownish-gray. Both mercuric chloride and potassium hydroxide are listed as negative. The hardness is high, being 5.5 and the mineral is brittle. Its color is pitch-black to greenish and streaks greenish-brown to black. It exists in massive form but may also be botryoidal.

In the category of microscopic determination is etch-figure analysis. Etch figures are definite shaped solution cavities formed by momentary or prolonged action of a natural or artificial solvent on crystal faces, the configuration and distribution of which are related to the solvent and the molecular structure of the face on which they occur.

The first application of the method was in 1808 by Widmannstätten who noted the characteristic markings produced on the faces of meteorites by the action of acid. This investigator noted that the etching so produced is definitely related to the molecular structure of the iron in the meteorite. Etch-figure analysis has been treated extensively by A. Honess (1927). According to Honess the nature and origin of etch figures from solvent action on the plane surface of crystals is definitely related to the molecular structure.

The etch method, like other methods for the determination of crystalline properties, sometimes conflicts with the more objective methods, e.g., X-ray spectroscopy. In most cases the apparent discordances have not been satisfactorily explained. Etch figures may be photographed, reproduced by ink impressions, or may be examined with a reflecting goniometer.

Crystals that are simple and lustrous are usually chosen for etch analysis since these produce best results. Generally, the

treatment is with an acid in a range of concentrations and at varying temperatures so that the optimum conditions are found. Solvents must not have an action which results in deposition of insoluble materials on the surface of the specimen (e.g., alkalis on uranyl compounds, i.e., secondary uraniferous minerals).

The procedure is to immerse the specimen repeatedly in the solvent, short duration being preferable to prevent multiple layering and chaotic intergrown hillocks. The microscope is used to inspect the results. Reagents which may be used are: aqua regia (e.g., pitchblende); nitric acid (e.g., autunite); hydrochloric acid; water (e.g., dakeite); hydrogen peroxide (e.g., dakeite); citric acid solution; ammonium chloride solution; or, a mixture of potassium bisulfate and calcium fluoride, this being used as a solvent while fused. Others may be used, their type depending on the particular specimen under examination.

Natural surfaces are more desirable than a polished section because it is difficult to obtain a plane as true as the natural surface which would produce reliable or reproduceable results. Vicinal faces and striations, if present, should be studied in conjunction with the etchings to insure proper symmetry interpretations. Fred S. Young (1941) has had success in cutting and polishing uraninites, and some of the secondary uranium minerals such as autunite and gummite, for examination.

Polarographic Analysis

Investigations on the polarographic measurement of uranium were made in 1938 by R. Stubl. This investigator found that the reduction potential of trivalent iron is so close to the reduction potential of the uranyl ion that to determine uranium in the presence of large amounts of iron it is neces-



The Fisher electropode, an instrument based on the dropping mercury electrode principle of analysis, is suitable for the analysis of uranium by the technique of Stuhl.

sary to reduce the concentration of the uranyl ion to a relatively small value.

This is done by production of a complex ion since otherwise there will be interference and the polarographic waves of uranium will be masked. When, in the absence of oxygen (air), a solution of ammonium carbonate is added to a solution of uranyl ions and the polarographic curve registered after each addition of the carbonate, it will be found that two distinct polarographic waves will be obtained.

One has the half-wave potential at -0.83 volt. This corresponds to reduction at a potential of -1.45 volts. If all the trivalent iron present in the solution is reduced to the bivalent state, by means of a hydrochloric acid solution of hydroxylamine, the polarographic determination can be made for the uranyl ion.

The hydroxylamine in acid solution is a satisfactory reducing agent for copper, bismuth, antimony, tin, lead, thallium, cadmium, titanium, and zinc ions in the presence of trivalent iron. All ions which are reduced to metal and deposited by the dropping-mercury electrode at potentials of between 0 and -1.0 volt may be determined polarographically in the presence of iron. The method may be useful for determining the adsorbed constituents of ferric hydroxide precipitates.

Chromatographic and Capillary Analysis

Chromatographic selection is useful for separating uranyl salts from other components in a complex system which does not respond to other methods of analysis. It is especially useful in mixtures with organic substances for determinations which depend on color or fluorescence and which would otherwise be masked. Chromatographic and capillary analysis are excellent for manipulation of very small quantities of speci-

men and are important when used in conjunction with ordinary chemical tests.

W. G. Brown (1939) described microchromatographic analysis for use as an adjunct to the Twsett Column. The apparatus consists of two glass plates six inches square, the upper one of which has a one-fourth inch hole in the center. Between these plates a piece of absorbent paper of the same area is placed. Other materials may be substituted for the paper, this depending on the test made. Through the hole in the top plate the solution to be examined is poured and after a short time the developing solute is added.

The chromatogram generally consists of concentric rings which may be further treated or may be kept as a permanent record obtained provided alteration does not occur when exposed to the atmosphere. This form of analysis may be of value in resolving ores which contain several uraniferous minerals.

In 1939 W. Hoffmann described ultraviolet chromatography. In this the chromatogram or adsorbent column is examined in ultraviolet light, fluorescence being the identifying criterion. Since uranyl salts are intensely fluorescent such procedure may be of value in research or elsewhere with minerals which are to be resolved or compared.

A chromatographic test is in the application of a dye-system to uranium minerals, i.e., a mixture of reactive dyes selective adsorption and diffusion processes occur, as well as chemical reaction, with subsequent examination under ultraviolet radiation. Long wavelength radiation is preferable since large organic molecules are best excited by this type of light. In this way otherwise identically appearing specimens may sometimes be differentiated. Feigl pointed out that large organic molecules, e.g., dyestuffs, are more adapted to chromatographic separation and capillary analysis than most

other types of molecules, hence the use of mixtures of organic dyes of complex nature.

Related to chromatographic analysis is capillary analysis. In the latter technique the components of a solution are separated by adsorption and/or diffusion actions which occur when a solution is allowed to pass through a substance. The separation results from the surface energy, due to interfacial tension, seeking equilibrium.

An example of capillary analysis is in solutions containing the soluble portions, e.g., water-soluble uranium compounds which often exist together, one resulting from a reaction which involved the other. Another example is in the separation of alpha and beta uranyl compounds or uranyl compounds. These would accumulate in certain regions of the absorbent, e.g., on strips of paper as zones or bands. Adsorption is the term applied to the changes of concentration of material at an interface. An interface is the boundary which exists between two different phases.

Feigl (1940) has discussed diffusion and/or adsorption phenomena which occur when solutions containing several materials are placed on spot paper. In this a segregation may occur in the paper through which the liquid has passed.

Goppelsroeder (1910 and on) used capillary analysis with many important applications resulting from the investigations. The procedure is to suspend strips of paper vertically, under controlled conditions, with one end immersed in the solution. The liquid passes up the strip and the components separate by the previously described mechanisms.

Danckwortt and Pfau, and the present writers, applied capillary analysis to fluorescence analysis with extraordinary results. The limits of detection for a number of materials were extended considerably when the paper was examined in ultraviolet radiation. The fluorescence characteristics of the uranyl ion makes this form of testing particularly suited to

the study of minerals and uranium compounds. An added mode of testing lies in the direct application of chemical reagents used in spot tests to the various zones on capillary paper after the components have been separated.

Of especial value in fluorescence chromatography and capillary analysis of uranium is the use of *black* adsorption media or paper. This follows from the contrast of the uranium yellow-green fluorescence and/or color on a black background. Likewise, the use of a black background to inspect tubes of uranium solutions for yellow coloration is of practical significance. This holds for tubes which are being inspected under ultraviolet light for the characteristic yellow-green fluorescence. It also holds for tubes which are being examined under white light.

In the iron test using potassium ferrocyanide the metal ions are adsorbed on stannic acid gel, traces being revealed in smaller quantities than is possible by solution methods. This can be extended to other ions, including those of uranium, as an important means for localizing material in the search for traces. The basic facts involved were first pointed out in 1913 by W. Mecklenburg who showed that a dilute solution of titanium, in which the titanium could not be detected by hydrogen peroxide, produced an excellent titanium test by the pertitanate reaction provided the solution was boiled with stannic acid gel, filtered, and the reaction applied to the gel.

The applications of detection of traces of metals after localization by adsorption appear to be of significance. Metal ammine ions are more greatly retained by silica gel than the corresponding metal ions. This is directly compatible with information presented in the section on amines as precipitants (cf. previous chapter on the ammines of uranium).

The foregoing information is of very much interest when it is realized that the extremely minute amounts of uranium which can be isolated on gels may be incorporated into a

phosphor, e.g., with sodium fluoride, and subjected to fluorescence analysis. This places the analysis on a basis where results are interpreted in number of molecules rather than in terms of gammas. It would be desirable to use a gel which could be ignited at relatively low temperatures in order to leave the adsorbed uranium in the residue.

I. Langmuir (1940) has described a method similar to the above. The method is for determining the presence or absence of small amounts of a substance suspected but not known to be present in a carrier medium. It involves forming, on a relatively smooth, reflective base member, such as one of metal or glass, a film of successively applied monolayers. These include a surface monolayer of a material adapted selectively to adsorb the substance for which the test is being made. It includes an observable alteration in the properties of the film and then exposing the film to the action of the material under test.

In the summation of a number of studies on capillary analysis Feigl obtained conclusions which may be advantageously applied to both capillary study and chromatographic investigation. The following facts probably hold to a varying degree for the adsorbents, e.g., magnesium oxide, calcium carbonate, and others, in chromatography.

The rise of solutions in paper and the diffusion of drops of solution through paper can result in separation of the solvent and the solute (and the solute from other solutes as well as from solvates) in the same system. The causes for this segregation are diffusion and adsorption mechanisms.

Filter paper exhibits selective adsorption toward dissolved materials and since these travel to varying degrees in paper their separation may be effected. If water is the solvent a greater diffusion rate and a smaller passive adsorption capacity than that of the solutes will occur, the result being that

water will precede the dissolved materials in capillary ascent.

The size of the water rings of the zones formed on paper by the solvents and solutes is a function of the concentration, the size of the ring increasing with a decrease in concentration. Therefore, the nature of the solute, as well as the solvent and the concentration regulate the height and the time required for ascension and separation. Chemically similar substances will rise to the same height if in equimolar concentration.

The basis for results lies in the varying distances to which the ascension occurs, greater differences being noted with mixtures of organic dyes than with mixtures of inorganic molecules. In addition, a quantitative separation of the components is never completely accomplished. A dissolved material remains isolated only in the outermost zone and in other parts of the paper, after passage of the solution, the components exist in varying amounts.

The adsorbability of an electrolyte is repressed by its common ions, a fact which may lead to specific application in identification of certain ions provided the electrolyte is known. Solutions containing a number of salts which produce ions do not impair the passive adsorption of the individual components.

For the examination of quantities of uranium solution as small as 0.005 milliliter a combination of adsorption on a suitable substrate and inspection with a luminescence microscope is quite often useful. It has been pointed out by several investigators that the fluorescence of materials is much greater when they are adsorbed in a very finely divided state on adsorbents than when they are in solution, or when coarsely dispersed. Uranium which has been adsorbed through application to the medium in solution form may be examined when dry or may be inspected after moistening

with a solution of anions of the fluorescence enhancing type. The accompanying table lists adsorption media suitable for use in this procedure.

ADSORPTION MEDIA FOR FLUORESCENCE ANALYSIS
OF URANIUM IN MICRO-LITER AMOUNTS OF SOLUTION

White

Cotton
Kaolin
Chalk
Magnesia

Black

Charcoal
Black paper
Clay
Lampblack

SPECIAL METHODS IN URANOMETRY

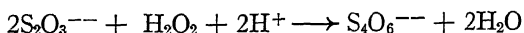
WHILE doubtless there are instances where so-called super-sensitive tests for uranium are a disadvantage, the use of special reactions is of the highest order of importance in many cases. Sensitive reactions render valuable services in research, the latter term often implying the use of more than usual care in detection and demonstration of traces. In systematic analysis specimens which otherwise show no extreme differences can be resolved by employing sensitive reactions.

The need for new and distinctive tests for uranium has been pointed out in the previous chapter. This need is re-emphasized because of the constantly changing field of application. This is evident for uranium by the unique and topmost place it occupies among the natural elements; and, by the many properties which lead to developments which engage both chemists and physicists. And, many ramifications ensue because the methods of chemists and physicists, many times different in both type and form, often disagree. The information which follows, like the foregoing data, may point toward needed new and distinctive tests mentioned above.

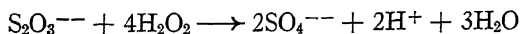
Fortunately, from an analytical standpoint, a peracid of uranium exists (see a previous chapter). The peracid group, $-O-OH$, has a specific action which leads to important applications in the detection of small amounts of the element characterized by such formation. Although the *peracid reaction* probably has not been heretofore applied to uranium (although it has been used for Mo, Ti, W, Cr, and others) its use for the detection of this element may be more important than its use for the detection of the other peracid formers.

The peracid formers catalyze the reaction between hydro-

gen peroxide and sodium thiosulfate in acetic acid. In 1913 Abel showed that the reaction between these substances normally proceeds according to:



Abel showed that this reaction follows an entirely different course when molybdates are present:



Tungstates, vanadates, titanium, and zirconium salts, as well as molybdates were shown by Feigl to direct the reaction according to the second mechanism.

Peracids, H_2MoO_5 ; H_2TiO_4 ; and peruranic acid behave in several reactions in such a way that exceedingly small amounts may be detected by their catalytic action or in inducement of reactions to proceed along certain lines.

The application of characteristic peracid reactions to uranometry has been made by one of the present writers (J. D.). The following reagent may be used to detect peracids. It is called Feigl's Reagent and is so sensitive to the presence of elements which are peracid formers that merely stirring with a tungsten wire (W is a peracid former) will evoke a positive reaction.

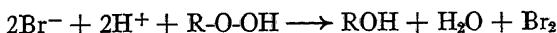
Feigl's Reagent is prepared by mixing equal parts of the following solutions which have been freshly prepared. The first solution consists of one gram of hydrated sodium thiosulfate in 100 cc. of water. The second solution is prepared by dissolving 0.6 gm. of hydrated barium chloride in 100 cc. of 1/20 normal acetic acid. The third solution contains 0.7% hydrogen peroxide in 100 cc. of water. One volume of the respective salt solution is added to one volume of the reagent solution. The reagent solution, when added to water as a control remains unchanged (clear) for about 15 or 20 minutes, but the addition of peracid formers produces a tur-

bidity because of the precipitation of barium sulfate, in a period as brief as 5 to 8 minutes.

Another reaction in which the peracid group plays a part is in the ability to liberate bromine instantly from acidulated alkali bromide solutions. The presence of dilute hydrogen peroxide does not cause this to occur. The presence of the $-O-OH$ group is not necessary for the production of the reaction provided the element is present along with hydrogen peroxide.

A fresh one per cent solution of sodium thiosulfate will precipitate barium sulfate, the reaction being catalyzed by very small amounts of peracid forming elements. As little as one part of columbium in 20,000,000 will evoke this reaction, limits for other elements being of a similar magnitude. The actual amount of peracid forming elements in several cubic centimeters of solution which will produce a reaction ranges from 2 gammas to 0.2 gamma.

Feigl and Demant (1937) used another reaction to detect the peracid forming elements. In the reaction the activation of hydrogen peroxide-bromide ion system by the peracid can be used for detection provided an indicator is present. The reagent consists of a mixture (fresh) of hydrogen peroxide, potassium bromide, and methyl orange which has been acidified with sulfuric acid. The red solution is decolorized on the addition of the peracid formers because of the liberation of bromine which acts on the indicator with the reformation of the bromide ion:



Facts of considerable interest may be as follows. The action of nascent bromine on fluorescein at pH 5.5 is to convert the fluorescein into eosin. Hahn (1933) and Ganassini (1904) showed that this may be used as a test for bromides in quantities as small as 10^{-6} gram. The test functions satis-

factorily in the presence of chlorides. Radley and Grant (1933) have described this reaction. The reaction is best carried out with a piece of filter paper which is impregnated with a solution of fluorescein and dried, the bromide being mixed with acetic acid and lead dioxide, and heated in a test tube. The neck of the test tube is drawn into a fine capillary and the small open end placed in contact with the test paper. For modification to the peracid test apparatus is specially constructed so that the liberated bromine impinges on fluorescein paper.

The application of fluorescent indicators and the exceedingly delicate methods of fluorescence analysis to the peracid reaction is indicated for elements other than uranium. Fluorescent indicators are much more sensitive under certain conditions than are the ordinary indicators. The accompanying table lists a number of extremely sensitive fluorescent indicators.

FLUORESCENT INDICATORS SUITABLE FOR HALIDE-PERACID INVESTIGATION

Rhodamine
Resorufin
Fluorescein
Acridine
Benzoflavine
Acridine Picrate *
Dichlorofluorescein
Beta-methylumbelliferone

* This substance is obtainable from Dr. W. S. Guthmann of *The Edwal Laboratories* in Chicago, Illinois.

The applications of fluorescent indicators to the peracid reaction, especially for uranium, is in the quenching or inhibiting action possessed by halogen ions, e.g., bromine, liberated during a peracid reaction. The quenching or inhibiting action

implies that the fluorescence of a substance, generally in solution, is decreased or removed entirely.

Very small amounts of substances will exert a quenching action on uranium solutions. That the halogen ions frequently act as inhibitors of fluorescence was pointed out in 1935 by E. Schneider. Resorufin fluoresces yellow in ultra-violet radiation. An alkali carbonate solution of resorufin is quenched by the action of bromine ions (H. Eichler, 1934).

In *Hackl's test* for uranium the uranyl ion reacts with hydrogen peroxide in alkaline solution to produce a yellow coloration with as little as 0.2 mg. of uranium. This test is of value in confirmation of precipitates and for filtrates obtained during the course of analysis. Detection is performed on a spot plate. Chromium must be absent although the slight interference by other elements, e.g., molybdenum, vanadium, and cerium is practically nil. In an acid solution a test for titanium is obtained.

Whenever the ore is fairly uniform and the gangue is of nearly constant composition, the approximate quantity of uranium present can be determined by the *specific gravity method*. The specific gravity of an ore is determined quickly by dividing the weight of a quantity of ore which will displace a certain amount of water, say 300 to 500 cc., by the weight of the water.

Knowing the specific gravity and composition of several specimens, a table may be prepared to give the quantity of uranium for each specific gravity determined. The table is, of course, dependent on the individual ore examined.

An exceedingly sensitive test for a number of anions and cations was originated by one of us (J. D.) and used as early as 1931. The method consists of the addition of very pure lumps of *calcium carbide* to aqueous solutions containing the ions. The voluminous precipitate of calcium hydroxide

(+R acetylenide) which is thrown down is colored characteristically according to the ion(s) present in the system.

Solutions containing copper, lead, chromium, or others produce dark-brown (Cu); black (Pb); orange-yellow (Cr) in extremely dilute solutions (see the accompanying table). Ions which form a dark colored precipitate interfere with reactions which evoke lightly colored precipitates. A large number of elements and their ions may be identified in this manner, e.g., different valence states for the same element will form dissimilar coloration on the calcium hydroxide precipitate.

Uranyl ions color the calcium hydroxide a characteristic yellow. A bright yellow turbid coloration is noted in a neutral solution containing 10 mg. of uranium in 30 cc. of liquid. A discernible yellowish color has been obtained with as little as 0.40 mg. of uranium per 10 cc. of solution. The concentration, pH, temperature, purity of the reagent (CaC_2) and the presence of other ions and their concentrations, determines to a large extent the type of coloration which will be produced in this system of analysis. Other carbides may be used instead of the calcium compound. Chromium and cadmium form yellow colors but these are slightly different than the hue produced by uranium. A control reaction with the reagent alone should produce a pure white precipitate of calcium hydroxide.

The *addition of hydrofluoric acid* in excess to reduced uranium salts produces a heavy green precipitate which can be washed with an aqueous solution of hydrofluoric acid. After ignition the uranium may be assayed as U_3O_8 (Giolitti).

Beta-oxime of isatine is the reagent used by V. Horovka and V. Sykoka (1938). The procedure is as follows. To the uranyl ion solution containing the equivalent of 0.002 to 0.3 gram of urano-uranic oxide in 100 ml. of water at 100°C . add 5 to 60 ml. of a one per cent solution of the oxime. Re-

ANALYSIS BY CALCIUM CARBIDE REAGENT

<i>Cation</i>	<i>Coloration</i>
UO ₂ ⁺⁺	Bright yellow *
Al ⁺⁺⁺	Grey-green
Cu ⁺⁺	Brownish-black
Cd ⁺⁺	Canary yellow
Pb ⁺⁺	Black
Co ⁺⁺	Blue-grey
Fe ⁺⁺	Blue
Fe ⁺⁺⁺	Gold then green
Ni ⁺⁺	Blue then black
Nd ⁺⁺⁺	Rose

* Fluorescent after expelling the water by moderate heat treatment and excitation by ultraviolet radiation of $\lambda = 2537$ A.U.—after acid treatment.

move from the hot plate and add 5 to 10 ml. of a 10% sodium acetate solution. An excess of both reagents is required but the orange-yellow precipitate cannot be obtained from uranyl nitrate solutions except after buffering with acetate. After allowing to stand for 2 to 3 hours filter and wash with 20 to 100 ml. of hot water. Ignite and weigh as U₃O₈.

When *acetoacetanilide* is dissolved in methanol a clear colorless solution results which has an intense bright blue fluorescence. On the addition of uranyl salts a deep orange coloration is produced which appears cherry-red in long wavelength ultraviolet light. Likewise, when beta-methyl umbelliferone is dissolved in methanol a clear colorless solution is formed, this having a brilliant blue fluorescence. This reagent, on addition of a uranyl ion solution, forms a clear light yellow-orange solution which rapidly changes to a mass of pale yellow needles which have an intense blue fluorescence. The yellow-orange solution first obtained during the course of the reaction is non-fluorescent.

Uranium may be determined quantitatively, when hexavalent, by use of 5% aqueous solution of *alpha*-quinaldic acid according to Ray and Rose, 1933 (cf. data in a previous section and the structure in the previous chapter).

A 2% aqueous solution of *sodium salicylate* forms an orange-red coloration with the uranyl ion and this may be used for the estimation of uranium. Errors by use of sodium salicylate may be as high as 7% although all the iron must be absent, the test being conducted in a neutral or slightly acid solution (Miller, 1919). The wet precipitate is not intensely fluorescent as contrasted to the extraordinary fluorophore-nature of both ions in other combinations.

Paraldehyde dissolves uranyl salts to form a solution with a bright yellow color and on addition of water a yellow-white turbidity is formed. Or, a reagent consisting of methanol containing paraldehyde dissolved in it may be used for this purpose. The addition of isopropylamine to this forms a bright orange-yellow precipitate.

Benzoin forms white precipitates with molybdates, tungstates, vanadates, and uranyl salts in mineral acid solution according to H. Knowles (1932).

The *thymol* tests may have possibilities for detection and determination of uranium. A saturated methanol solution of thymol reacts with uranyl salts to form a clear red-brown liquid, the color of which is destroyed by the addition of slight amounts of nitric acid. The addition of isopropylamine, however, to the coloration deepens it, forming an orange-brown hue while the addition of 2-amino-2-ethyl-1,3-propanediol forms a solution which has a rust color.

A yellow precipitate is formed when a 5% aqueous solution of *allylthiourea* containing 30% sodium hydroxide is added to uranyl salt solutions. A control must be used since cadmium and copper interfere (Lemaire, 1908).

John H. Yoe (1932) used the ammonium salt of aurintri-carboxylic acid for the detection of uranyl ions.

Test tube flame tests were described in 1936 by A. R. Clark. Uranium is included in the scheme of analysis.

Uranyl salts in neutral solution do not appear to react with highly concentrated (up to saturation) solutions of strychnine, morphine, or arecoline hydrobromide characteristically, according to unpublished studies by the present writers.

With the presence of ultraviolet light, and in acid solution, some of the *alkaloids* react with uranyl salts; an oxidative process. Strychnine in sulfuric acid is not affected by the addition of small amounts of uranyl acetate. However, on exposure to sunlight the solution becomes violet. According to J. Aloy, et al (1926) the method may be used for the detection of as little as 1×10^{-5} part of strychnine. Under the same conditions of light exposure and solution properties, codeine and morphine give deep blue colorations. None of the common alkaloids give similar reactions.

If the solution of uranyl acetate is exposed singly to sunlight and then added to the acid solution of the alkaloid, a blue color can be produced. This is due to the catalytic effect of the uranium on its solution, leading to the formation of formaldehyde which is evidenced by reaction with codeine, and forming a blue coloration. These facts may be of utility in the detection of small quantities of uranium. Iron gives a similar reaction.

Extremely small amounts of uranium can *photosensitize* a reaction. The catalytic effect of uranium for leading a reaction to completion has been used in several industrial processes. A number of reactions are known which will not proceed unless exposed to light, along with the presence of small amounts of uranium. The accompanying table gives several reactions dependent on the photocatalytic nature of uranium.

URANIUM AND ATOMIC POWER

REACTIONS PHOTOSENSITIZED BY URANIUM

<i>Reaction</i>	<i>Reference</i>
Oxalic acid from ether.....	Rowell and Russell, <i>J. Chem. Soc.</i> , 127, 2900 (1925).
Succinic acid and methylene blue..	Ghosh, et al, <i>Z. phys. Chem.</i> , B32, 163 (1936).
Photolysis of hydroxylic acids....	Neuberg, <i>Biochem. Z.</i> , 39, 158 (1912):
Oxidation of mandelic acid by Br.	Ghosh and Ray, <i>Z. phys. Chem.</i> , B32, 158 (1936).
Photo-oxidation of keto acids.....	Bauer, <i>Helv. Chim. Acta</i> , 19, 234 (1936).
Photolysis of dibasic acids.....	Fay, <i>Amer. Chem. Jour.</i> , 18, 269 (1896).
Photolysis of formic acid.....	Ghosh and Mittner, <i>Quart. J. Indian Chem. Soc.</i> , 4, 353 (1927).
Photolysis of halogenated acids...	Ghosh and Ray, <i>J. Indian Chem. Soc.</i> , 13, 1 (1936).
Production of Vitamin D.....	Pacini, A. J., <i>U.S.P.</i> 1, 880, 977-8.

Plattner's classical work on *blowpipe analysis* of minerals in about 1875 contained a rather extensive discussion of uranium minerals. The discussion is of unique interest from several aspects. Aside from being correct in most phases, except the chemistry, it may yet have value in its application to specific determination of minerals in the field. Plattner's methods for the blowpipe analysis of uranium minerals follow.

When testing for uranium the chief point to be considered is the behavior of its oxide with sodium phosphate, with which in the oxidizing flame it yields a yellow glass which turns yellow-green on cooling.

In the absence of other oxides producing similar colors sodium phosphate yields decisive results, but when oxides of iron and possibly also titanitic acid are present, the sodium phosphate bead in reducing flame becomes red on cooling (vide iron). The uranium color can only be perceived by treating the glass in an oxidizing flame, when it assumes on cooling a green color mixed with a large amount of yellow.

When there is little uranium present, and much iron, the fluxes show only the iron. The substance must then be treated with potassium bisulfate, ammonium carbonate, and so on (vide iron). Substances which contain oxides of copper and uranium yield green beads in the oxidizing flame with borax and sodium phosphate. As substances containing oxides of iron and copper, without uranium, do the same, the following method may be adopted to detect the presence of a small amount of uranium. The substance is treated with sodium carbonate, sodium borate, and a silver button on charcoal in a reducing flame until all of the copper is reduced into the silver. After this the slag, containing uranium and other non-reducible oxides is dissolved by warming with a small amount of aqua regia. The solution is treated with an excess of ammonium carbonate and the process conducted according to examination for iron.

Uranium minerals have blowpipe characteristics which are interesting. *Uraninite* from Johann-Georgenstadt yields water at first. Then usually, if containing many foreign substances, a small amount of sulfur which sublimes after which the sulfide of arsenic appears and finally metallic arsenic. If the open tube evolves sulfurous acid fumes or if a ring of arsenous acid collects on the tube the assay does not alter perceptibly. The borax bead is only rounded somewhat on the edges and usually tinges the flame azure-blue (lead) near the assay, and a fine green at a greater distance (copper).

The thoroughly ignited mineral behaves with glass fluxes like the oxide of uranium which is shown in the accompanying table.

Sometimes uraninite is not dissolved by sodium carbonate so it is treated in the reducing flame on coal, which often causes a perceptible odor of arsenic. After washing away the coal-like particles and higher oxide of uranium it yields metallic particles of a light copper color. These consist of plumbiferous material since a yellow coat is formed on the coal.

Blowpipe Characteristics of Uranium Dioxide
After Plattner

Alone on charcoal—Infusible with oxidizing flame, but turns a dark yellow-green. Turns black under the reducing flame.

With borax on platinum wire—Under oxidizing flame acts like oxide of iron, but with lighter colors. The strongly saturated glass can be flame-enameled yellow. Under reducing flame acts like ferric iron. The green glass, saturated, can be flamed black.

With phosphate on platinum wire—Under oxidizing flame, dissolves to a clear yellow glass, which turns yellowish-green when cold. Same reaction under the reducing flame, except the glass becomes more greenish. With tin on charcoal it becomes a dark green.

With sodium carbonate—Insoluble under the oxidizing flame, turns yellowish-brown. Same color under reducing flame; the uranium dioxide can not be reduced to the metallic form.

Coracite and *gummite* yield much water, otherwise they behave much like uraninite. The sulfates involving UO_2 yield water in the matrass, become red, then brown, and on coal evolve sulfurous acid. They react for uranium with the

fluxes. The sulfates involving U_3O_8 behave in a like manner but borax beads change to a brown or greenish black mass. The sodium phosphate bead with tin on coal is dark-red in the presence of copper. The nitric acid solution, when treated with water and ammonium hydroxide in excess yields a yellow precipitate (uranate). This behaves like pure UO_2 with fluxes although if copper is present the ammoniacal solution is blue. With sodium carbonate on coal all yield a strong sulfur reaction.

Autunite yields water and becomes opaque straw-yellow in the matrass. On coal it fuses with a slight intumescence to a black globule which has a crystalline surface. Uranium is demonstrated with glass fluxes and with sodium carbonate as a yellow unfused slag (Berzelius).

Torbernite behaves like autunite but shows copper with sodium phosphate and tin on reduction with sodium carbonate. The copper button is frequently whitened by arsenic and this may be recognized by its odor. *Liebigite* yields water and becomes greenish-gray in the matrass. At red heat this mineral blackens without fusing and becomes orange-red on cooling. On coal the mineral is infusible and remains black. With borax in the oxidizing flame a yellow bead is obtained. This is green in the reducing flame. The bead dissolves with effervescence in hydrochloric acid with a resulting yellow solution (J. L. Smith). The related *chalcolite* (uran-kalk-carbonate) loses water and becomes grayish-black, or in air is infusible and shows uranium with fluxes. *Voglite* blackens when heated and is infusible and colors the flame green. It yields copper when reduced with sodium carbonate.

Uranophane yields an alkaline solution in the matrass, blackens and cools to a rusty-brown. In the open tube it becomes almost orange-yellow, and when strongly heated yields a small amount of vapor and a coating, partly volatile and partly fusible to drops. The drops indicate the presence of

tellurium and a feeble selenium odor is often detected. When alone the mineral fuses to a black glass and imparts a slight copper coloration to the flame. On coal it affords antimony and bismuth while with the fluxes it shows silicon and uranium.

Riptographic analysis may have use in certain studies on the chemistry of uranium. The complex solution is analyzed by removing one of its components and then determining a physical property. This is repeated, a component being removed and a physical property determined until a set of values is obtained which can be plotted. The resulting graph will give indications as to the constituents of the system as well as the purity and other properties.

Uranium produces a brown coloration when mixed with *dioxymaleic acid* according to H. J. H. Fenton. A violet coloration is formed when uranium reacts with alizenesulfonic acid (cf. alizarin) according to V. de Boer.

Attention is directed to Frequency of Occurrence data elsewhere. When examining specimens of uraniferous minerals it is often of aid to depend on the probability that the sample may be of a certain kind. Such information often leads the way in analysis and may expedite the assay.

Aqueous solutions of uranyl nitrate undergo a change in *surface tension* when exposed to light. By placing a drop of the liquid in a horizontal capillary tube and exposing one meniscus to light from a mercury arc the increase in surface tension can be determined by the increase in motion toward the lighted end. Grumbach and Schlivitch (1925) found this value to be of the order of 0.1 to 1 mm. per hour for aqueous solutions of sodium naphthionate. Solutions of fluorescein, sulfofluorene, xylene solutions of anthracene, and alcoholic solutions of xylene and gasoline behave in a similar manner. Solutions of ferric chloride and oxalic acid do not. This mechanism appears to have some connection

with fluorescence, if appraisal can be made on the basis of the preponderance of fluorescent, i.e., photodynamic, substances which are unique in this respect, e.g., uranyl nitrate, fluorescein, anthracene, and sodium naphthionate, etc.

A deep red-brown or brown coloration has been observed by the present writers to be formed when uranium reacts with certain organic substances. In some instances this coloration is produced by very small quantities of uranium, a fact which can serve in colorimetric analysis of the element. The following table lists several materials of this sort.

URANIUM REAGENTS FORMING RED-BROWN END-PRODUCTS

Ascorbic acid
Many salicylates
Meta-cresol
Ortho-cresol
Para-cresol
Dioxymaleic acid
Butyryl pyrogallate
Many phenols

Formerly the use of the *mass-spectrometer* was limited to only a few laboratories by the intricate and expensive equipment required. The availability of mass-ray analysis has increased with the introduction of low cost instruments such as that developed by A. O. C. Nier. The inexpensive instrument is suited to investigation over a wide field on plant and animal physiology and for other special studies where the isotopic constitution of matter is involved. The low cost mass-spectrometer consumes only a few watts of energy, as contrasted to the several kilowatts of power used by ordinary instruments, but requires the same amount of equipment also needed for the ordinary device.

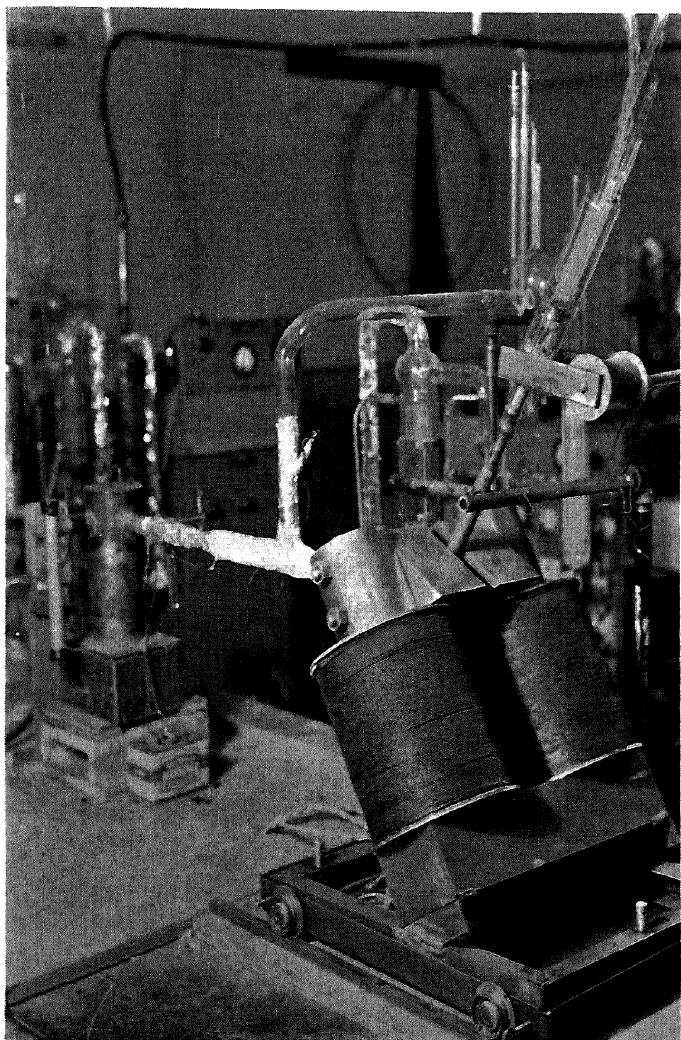
An interesting approach by indirect means for testing carnotite for the presence of uranium and radium is by

vanadium analysis. In carnotite the three elements, vanadium, uranium, and radium are invariably associated. When physical or other characteristics indicate that the specimen may be carnotite it is sometimes more convenient to test for the presence of vanadium, thereby indirectly demonstrating the presence of the other two. The test is far from infallible, however, since a positive reaction for vanadium does not conclusively establish the presence of uranium. Vanadium exists in a number of ores without the presence of uranium, and when other properties indicate uranium the test may then be made.

Vanadium tests may be used to corroborate other tests when uranium and/or radium are shown to be present. A positive vanadium test in the presence of uranium would demonstrate that the specimen is not pitchblende or uraninite but likely is carnotite although here again the evidence is not always absolute.

Vanadium may be detected in high grade minerals by moistening the specimen with a drop of hydrochloric acid. A deep red, which rapidly changes to green indicates vanadium. The same test may be applied by placing a few fragments of the sample in a small beaker and adding concentrated hydrochloric acid. The deep red color forms at once with most vanadium minerals, but the red soon changes to a deep green color, especially on heating. Hydrogen peroxide, however, immediately restores the red color.

Another test for vanadium which may be used is the hydrogen peroxide test. The procedure is to add hydrogen peroxide to a strongly acid vanadium solution. Low concentrations of vanadium produce a light yellow to orange color while higher concentrations yield the deep brownish-red color of pervanadic acid. Small quantities of vanadium may be confused with chromium, iron, or titanium, and possibly with large quantities of molybdenum.



Nier's mass spectrometer for routine isotope abundance measurements. The ion source is at the upper left; the analyzer and magnets are at lower left. In mass-spectroscopy only a small amount of material is necessary for analysis. (Photo: Dr. Alfred O. C. Nier).

Vanadium may be distinguished from chromium by adding ether to the solution after the addition of hydrogen peroxide. Chromium colors the ether solution blue while vanadium yields the same yellow color found in the aqueous solution. The yellow color due to iron may be destroyed by phosphoric acid and the titanium compound is easily destroyed by ammonium fluoride or hydrofluoric acid. Any yellow or brown-red coloration which persists after the addition of these reagents is due to the presence of vanadium.

In the table of radioelement ratios given in a previous section the ideal ratio between uranium and vanadium in carnotite or tyuyamunitite has been stated as 3.09. The approximation of 3:1 may be used if quantitative vanadium analysis has been performed for special reasons.

Another indirect method for indicating the presence of uranium in naturally occurring substances may be used. Instead of detecting vanadium the procedure is to demonstrate the *presence of radium*. The use of electroscope and Geiger-Mueller Counters has been discussed in a previous section. Determinations may be made by these means; however, the fluorescence excited by the radiations from radioelements may be used for purposes of detection. Devices which depend on luminescent effects are of two kinds, i.e., the spinthariscopes and the radioscope. In these instruments scintillations are produced by impingement of alpha particles on a zinc sulfide screen. The spinthariscopes are not as effective as the radioscope. In the latter the ore is powdered and macerated with water. This releases the solid of its emanation. The emanation disintegrates with the production of alpha particles and other radioelements, producing scintillations on the screen. Bright flashes are produced on the zinc sulfide-phosphor screen by radium and uranium, or, thorium.

Three methods for the detection of uranium because of its radioactive nature due to the presence of radium are

(1) electroscope or counter techniques which depend on ionization, (2) spinthariscopes and radiosopes which depend upon fluorescent effects, and (3) the actions which occur in cloud chambers. In the cloud chamber the tracks formed by the alpha particles are characteristic and these may be used as the determining criterion. Chambers large enough to permit introduction of gram sized specimens, show numerous alpha tracks. From one gram of uranium, 24,770 alpha particles are emitted every second.

Radiochemical methods for uranium studies are suggested. The technique consists of preparation of a radio-colloid (generally as a radiosuspensoid; solid-in-solid system) of the extracted mineral specimen and recording the results photographically. O. Hahn (1936) used artificially prepared crystals of ammonium bichromate, sodium bromate, and others, which contained radium, thorium, and related elements to complete the colloid. These crystals produced characteristic radiographs due to the variable distribution of the radioelement.

L. Zill, in collaboration with the present writers, studied radiocolloids which contained traces of uranium. Unweighable amounts of radium-free uranium were distributed in large single crystals of 2-nitro-2-methyl-1, 3-propanediol and 2-nitro-2-ethyl-1, 3-propanediol. A radiosuspensoid consisting of artificially prepared trigonal crystals of sodium nitrate showed discontinuities in distribution of the uranium.

According to O. Hahn (1936) the detectability of chemical elements by means of their radioactive isotopes may be expressed by stating the amount, by weight, of the active atomic type that emits as many particles per second, i.e., 3.7×10^6 particles, as does 0.1 milligram of radium. Such a comparison of atomic types with radium is given in the accompanying table, values corresponding to 0.1 milligram of radium. Since 0.1 milligram of radium is extremely

radioactive, which may be readily measured, even by means of its gamma radiation, it is apparent from the table that the amounts by weight of the chemical elements, which can be readily determined radioactively by means of their active isotopes, are exceedingly small.

The starting materials required for studies in the radiochemistry of uranium are: uranium X_1 ; uranium X_2 ; and, uranium Z. In the preparation of uranium X_1 concentrates must be prepared and from these the pure substance is then obtained. The concentrates may be obtained through fractional crystallization of large amounts of uranyl nitrate from water. The uranium X_1 concentrates in the mother liquor. Uranium X_1 may be concentrated in another way. Uranyl nitrate, the hydrated form, is shaken with ether. Two layers form, the aqueous layer of which contains nearly all of the uranium X_1 with little uranium and the ethereal fraction which contains the greater portion of the uranium.

RADIOACTIVE ATOMIC TYPES SUITABLE FOR COMPARATIVE APPLIED RADIOCHEMISTRY

Modified, after O. Hahn

<i>Element</i>	<i>Radioactive Atom</i>	<i>Amount, MGM.</i>
Radium.....	Radium.....	0.1
	Thorium X.....	6.2×10^{-7}
Thorium.....	Uranium X_1	4.4×10^{-6}
	Radiothorium.....	1.2×10^{-4}
Protoactinium.....	Uranium X_2	1.4×10^{-10}
	Uranium Z.....	5.0×10^{-8}
	Protoactinium.....	2.0

The preparation of comparatively pure uranium X_1 from concentrates is accomplished by use of ferric hydroxide as a scavenger. The procedure is to add a few milligrams of ferric chloride and the uranium and uranium X_1 which are subsequently precipitated with ammonium hydroxide. The

ammonium uranate is dissolved by heating with ammonium carbonate solution to 60° C. By this treatment the iron and the uranium X_1 flocculates after standing on a waterbath for some time. The precipitate of ferric hydroxide is filtered off and further purified, if necessary, by hydrochloric acid. The uranium X_1 is carried in the ferric hydroxide precipitate.

The thorium isotope (uranium X_1) has a half-life of 24.5 days. It is more applicable to radiochemical studies than the protoactinium isotopes, viz., uranium X_2 and uranium Z. Uranium X_2 has a half-life of 1.14 minutes and is useful in relatively simple radiochemical experiments because in 10 minutes after its isolation (it is carried down with UX_1) from its mother substance (UX_1) only a very small fraction of the initial amount remains. Uranium Z has the very convenient half-life of 6.7 hours but is difficult to prepare in large amounts since it is a branch product of UX_1 existing to the extent of only 0.3% in the latter radioelement.

Mention should be made of probably the most sensitive method for the detection of uranium that exists. This, unfortunately is not adapted entirely to application by man but lies in the realm of nature. Uranium, being a radioelement, may often be included in mica as fine particles of a relatively pure salt. When particles of a radioelement are sealed this way for long periods they continue to give off their radiations and inert radioactive gases which result from their natural disintegration.

The result of this process is the formation of the well known *pleochroic halos* about the particle of radioelement salt. Almost infinitesimal amounts of a radioactive material will, over a period of many hundreds of thousands of years, form pleochroic halos. Although it is not generally known the pleochroic halo method of detection of radium, for example, far surpasses the most sensitive man-made methods, including electroscopes and counter devices. It is probably

this way with uranium whose formation of halos would require longer and occur to a less extent. Pleochroic halos from radium may be formed by amounts as small as 10^{-17} gram, quantities which are well below the threshold limits of detection by electrical instruments.

O. Hahn (1936), commented upon some of the interesting aspects of pleochroic halos. He considers pleochroic halos from the following aspect: When a radioactive substance is not embedded in a crystal, but is adsorbed by minute particles in a liquid or a gas, it is possible to determine directly the nature of the radioactive element (e.g., uranium) emitting the radiations, from their effects on a photographic plate.

In these it is noted that a number of dark circular figures of various diameters are registered on the photographic plate. The diameters of these circles are definitely characteristic of certain radioactive substances. This makes it possible to identify the radioactive element when perhaps a thousand or less atoms are present.

The circles, called radioactive zones, which are produced artificially, occur naturally in some minerals and are of prime significance. In pleochroic halos small circular images are particularly well developed in a fluorite from southern Germany. The colored medium in this case is the decidedly less sensitive rock in place of a highly sensitive photographic plate. The halos appear as a number of concentric circles, each one corresponding to a particular one of such decomposition products as are found in uranium and thorium minerals. The interruption of the circular area by brighter annular bands results because the radiations are most effective at the respective limits of their so-called "range." Minute traces of radioactive minerals embedded in the inactive fluorite have sent their rays (alpha particles) into the surrounding mineral substance which they have colored.

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The Radioactive Minerals

The following list includes original and early papers. Names ascribed the minerals are, in many instances, those given by the original discoverer. It will be noted that a number are identical. Reference to the identity of radioactive minerals is not given here. Substances which have been found to contain uranium or other radioelements as traces have been included, as well as thorium-containing and rare earth minerals of import.

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- Annerodite—W. Brogger, *Geol. For. Forh. Stockholm*, 5, 354 (1881).

- Arrhenhite—A. Nordenskjold, *Geol. For. Forh. Stockholm*, 3, 282 (1872).
- Auerlite—Hidden, *Amer. J. Sci.*, 38, 479 (1889).
- Autunite—J. Berzelius, *Schweigger's Jour.*, 16, 244 (1816).
- Azorite—G. vom Rath, *Pogg. Ann.*, 113, 281 (1861).
- Baryta-autunite—F. Rinne, *Centr. Mineral.*, 618 (1901).
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- Bastnasite—W. Hisinger, *Svenska Akad. Handl.*, 187 (1838).
- Bassetite—A. Hallimond, *Min. Mag.*, 17, 221 (1916).
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- Cappelenite—W. Brogger, *Zeit. Kryst.*, 16, 468 (1890).
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- Caryocerite—W. Brogger, *Zeit. Kryst.*, 16, 87 (1890).
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- Chrysocolla (radioactive)—*Amer. Min.*, 10, 135 (1925).
- Clarkeite—Ross, *Amer. Min.*, 16, 213 (1931).
- Cleveite—A. Nordenskjold, *Geol. For. Forh. Stockholm*, 4, 31 (1878).
- Columbite—Ellsworth, *Amer. Min.*, 12, 368 (1927).
- Columbite-tantalite—*Amer. Min.*, 13, 556 (1928).
- Curite—A. Schoep, *Ann. Soc. Geol. Belg.*, 33, 558 (1924).
- Dakeite—Larsen and Goyner, *Amer. Min.*, 22, 561 (1937).
- Davidite—Mawson, *Trans. Roy. Soc. South Australia*, 30, 191 (1906).

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Dewindite—*Amer. Min.*, **7**, 162 (1922).
Droogmansite—*Amer. Min.*, **11**, 168 (1926).
Dumontite—*Amer. Min.*, **10**, 131 (1925).
Ellsworthite—H. Ellsworth, *Amer. Min.*, **11**, 332 (1926).
Endeolite—G. Flink, *Mejd. Gronland*, **16**, 234 (1898).
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Eschynite—Hofmann and Zerban, *Ber.*, **36**, 3093 (1903).
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Eytlandite—A. Nordenskjold, *Pogg. Ann.*, **11**, 280 (1860).
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Ferrothorite—*Amer. Min.*, **14**, 78 (1929).
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Flutherite—A. Weisbach, *Synopsis Mineralogia*, Freiberg (1875).
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Gilpinite—Larsen and Brown, *Amer. Min.*, **2**, 75 (1917).
Gummite—*Amer. Min.*, **16**, 215 (1931).
Hackmannite—*Amer. Min.*, **11**, 294 (1926).
Hagatalite—*Amer. Min.*, **11**, 137 (1926).
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Hagatalite—Kimura, *Japan Jour. Chem.*, **2**, 82 (1925).
Hjelmite—Katzer, *Oesterr. Zeit. Berg. Hutt.*, **57**, 313 (1909).
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Johnstrupite—W. Brogger, *Danske Vid. Selsk. Skr.*, 1 (1922).
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Lyndochite—H. Ellsworth, *Amer. Min.*, 12, 48 (1927).
Liebigite—J. Smith, *Amer. J. Sci.*, 5, 336 (1848).
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Mackintoshite—Szilard, *Le Radium*, 6, 223 (1909).
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Medjite—J. Smith, *Amer. J. Sci.*, 5, 337 (1848).
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Meta-autunite—F. Rinne, *Centr. Min.*, 618 (1901).
Meta-torbernite—F. Rinne, *Centr. Min.*, 618 (1901).
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Monazite—A. Levy, *Ann. Phil.*, 21, 241 (1823).
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Pilbarite—E. Simpson, *Chem. News*, 102, 283 (1910).
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Rogersite—*Amer. Min.*, 13, 207 (1928).
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Samiresite—A. Lacroix, *Bull. Min. Soc.*, 35, 87 (1912).
Schoepite—T. Walker, *Amer. Min.*, 8, 67 (1923).
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Sklowdowskite—V. Billiet, *Natuurwet. Tijd.*, 9, 25 (1927).
Soddite—A. Schoep, *Bull. Soc. Geol. Belg.*, 32, 345 (1923).
Synchisite—A. Nordskjold, *Geol. For. Forh. Stockholm*, 16, 336 (1894).
Schroekingierite—*Amer. Min.*, 20, 62 (1935).
Stasite—*Amer. Min.*, 7, 196 (1922).
Tanteuxenite—*Amer. Min.*, 13, 467 (1928).
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Thorotungstite—*Amer. Min.*, 13, 159 (1928).

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 Toddite—H. Ellsworth, *Amer. Min.*, 11, 332 (1926).
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 Tyrite—D. Forbes, *Phil. Mag.*, 13, 91 (1856).
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 Uranocircite—A. Weisbach, *Neues Jahrb. Min.*, 258 (1882).
 Uranokker—A. Werner, *J. Freiesleben Geol. Arb. Freiberg* (1818).
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Yttrfluorite—T. Vogt, *Centr. Min.*, 373 (1911).
Yttrogummite—W. Hidden, *Amer. J. Sci.*, **42**, 430 (1891).
Yttrilmenite—R. Hermann, *J. prakt. Chem.*, **42**, 11 (1847).
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Zippeite—*Amer. Min.*, **2**, 77 (1917).
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APPENDICES

Appendix I

VALUES OF SOME CONSTANTS

General Physical

Velocity of light.....	$c = 2.9978 \times 10^{10}$ cm./sec.
Definitive atomic weight.....	O(oxygen) = 16.0000
Atomic weight of electron.....	$A_e = 5.45 \times 10^{-4}$
Atoms per gram of hydrogen.....	$N = 6.017 \times 10^{23}$
Mass of atom of unit atomic weight.....	$M = 1.66 \times 10^{-24}$ gram
Mass of electron, i.e., also beta particle and positron.....	$m = 9.10 \times 10^{-28}$ gram
Mass of alpha particle.....	$= 6.59 \times 10^{-24}$ gram
Mass of proton.....	$= 1.66 \times 10^{-24}$ gram
Mass of neutron (representative).....	$= 1.00856$

Radium Constants

Half-decay period.....	$T = 1590$ years
Type of radiation.....	Alpha
Range of rays in air [STP].....	3.13 cm.
Number of alpha particles emitted per gram of radium.....	3.72×10^{10}
Helium generated per year per gram of radium.....	174 cubic mm.
Quantity of heat liberated by one gram of radium and equilibrium products per hour.....	136 calories

Absorption of Rays

Alpha rays completely absorbed by.....	0.006 cm. Al
Beta rays completely absorbed by.....	2 mm. Pb
Gamma rays half absorbed by.....	14 mm. Pb
Medium generally used for absorption of neutrons.....	water

Miscellany

1 kg. uranium contains approximately one-third mg. of radium.

1 short ton U contains 302.4 mg. Ra.

1 short ton U_3O_8 contains 256.58 mg. Ra.

1 short ton of 1 per cent U_3O_8 contains 2.5658 mg. Ra of which say 90 per cent (2.309 mg.) may be recovered, hence about 215 tons of 2 per cent U_3O_8 or 145 tons of 3 per cent U_3O_8 ore are needed to furnish 1 gram of Ra (P. M. Tyler).

Velocity of alpha particles, about . . . 1.922×10^9 cm./sec. (RaC')

Velocity of hard beta particles, about 2.9×10^{10} cm./sec.

Velocity of gamma rays, as great as .0.999c

Appendix II

INTERNATIONAL TABLE OF ATOMIC WEIGHTS 1941

J. Amer. Chem. Soc., 63, [3], (1941)

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Aluminum.....	Al	13	26.97
Antimony.....	Sb	51	121.76
Argon.....	A	18	39.944
Arsenic.....	As	33	74.91
Barium.....	Ba	56	137.36
Beryllium.....	Be	4	9.02
Bismuth.....	Bi	83	209.00
Boron.....	B	5	10.82
Bromine.....	Br	35	79.916
Cadmium.....	Cd	48	112.41
Calcium.....	Ca	20	40.08
Carbon.....	C	6	12.010
Cerium.....	Ce	58	140.13
Cesium.....	Cs	55	132.91
Chlorine.....	Cl	17	35.357
Chromium.....	Cr	24	52.01
Cobalt.....	Co	27	58.94
Columbium.....	Cb	41	92.91
Copper.....	Cu	29	63.57
Dysprosium.....	Dy	66	162.46
Erbium.....	Er	68	167.2
Europium.....	Eu	63	152.0
Fluorine.....	F	9	19.00
Gadolinium.....	Gd	64	156.9
Gallium.....	Ga	31	69.72
Germanium.....	Ge	32	72.60
Gold.....	Au	79	197.2
Hafnium.....	Hf	72	178.6
Helium.....	He	2	4.003
Holmium.....	Ho	67	164.94

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Hydrogen.....	H	1	1.0080
Indium.....	In	49	114.76
Iodine.....	I	53	126.92
Iridium.....	Ir	77	193.1
Iron.....	Fe	26	55.85
Krypton.....	Kr	36	83.7
Lanthanum.....	La	57	138.92
Lead.....	Pb	82	207.21
Lithium.....	Li	3	6.940
Lutecium.....	Lu	71	174.99
Magnesium.....	Mg	12	24.32
Manganese.....	Mn	25	54.93
Mercury.....	Hg	80	200.61
Molybdenum.....	Mo	42	95.95
Neodymium.....	Nd	60	144.27
Neon.....	Ne	10	20.183
Nickel.....	Ni	28	58.69
Nitrogen.....	N	7	14.008
Osmium.....	Os	76	190.2
Oxygen.....	O	8	16.0000
Palladium.....	Pd	46	106.7
Phosphorus.....	P	15	30.98
Platinum.....	Pt	78	195.23
Potassium.....	K	19	39.096
Praseodymium.....	Pr	59	140.92
Protoactinium.....	Pa	91	231
Radium.....	Ra	88	226.05
Radon.....	Rd	86	222
Rhenium.....	Re	75	186.31
Rhodium.....	Rh	45	102.91
Rubidium.....	Rb	37	85.48
Ruthenium.....	Ru	44	101.7
Samarium.....	Sm	62	150.43
Scandium.....	Sc	21	45.10
Selenium.....	Se	34	78.96
Silicon.....	Si	14	28.06
Silver.....	Ag	47	107.880
Sodium.....	Na	11	22.997

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Strontium.....	Sr	38	87.63
Sulfur.....	S	16	32.06
Tantalum.....	Ta	73	180.88
Tellurium.....	Te	52	127.61
Terbium.....	Tb	65	159.2
Thallium.....	Tl	81	204.39
Thorium.....	Th	90	232.12
Thulium.....	Tm	69	169.4
Tin.....	Sn	50	118.70
Titanium.....	Ti	22	47.90
Tungsten.....	W	74	183.92
Uranium.....	U	92	238.07
Vanadium.....	V	23	50.95
Xenon.....	Xe	54	131.3
Ytterbium.....	Yb	70	173.04
Yttrium.....	Y	39	88.92
Zinc.....	Zn	30	65.38
Zirconium.....	Zr	40	91.22

The following elements have not been adopted by the Committee on Atomic Weights. These, however, can be ascribed a position in the Periodic System of the Elements.

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Actinium.....	Ac	89	229
Alabamine.....	Ab	85	> 126
Illinium.....	Il	61	146 (?)
Masurium.....	Ma	43	> 54
Polonium.....	Po	84	218
Virginium.....	Vi	87	> 132
<hr/>			
Neutron.....	On ¹	0	1 ⁺

PERIODIC SYSTEM OF THE ELEMENTS

After, J. Amer. Chem. Soc., **59**, 219 (1937)

O	I	II	III	IV	V	VI	VII	VIII
R	RH R ₂ O	RH ₂ RO	RH ₃ R ₂ O ₃	RH ₄ RO ₂	RH ₃ I ₂ O ₆	RH ₂ RO ₃	RH R ₂ O ₇	RO ₄
He	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	
Ne	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	
Ar	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26
A	39.10	40.08	45.10	47.90	50.95	52.01	54.93	Co 27
18								Ni 28
39.944								55.84 58.94
							Br 35	
	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34		Ru 44
	63.57	65.38	69.72	72.60	74.93	79.2		Rh 45
								101.7 102.91 106.7
Kr	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	Ma 43	Pd 46
83.7	85.44	87.63	88.92	91.22	93.3	96.0		106.7
							I 53	
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52		Os 76
	107.880	112.41	114.8	118.70	121.76	127.5		Ir 77
Xe	Cs 55	Ba 56	* 57-71	Hf 72	Ta 73	W 74	Re 75	Pt 78
131.3	132.81	137.36		178.6	181.4	184.0	186.31	195.23
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84		
	197.2	200.61	204.39	207.22	209.00		85	
Rn		Ra 88	Ac 89	Th 90		U 92		
86		225.97		232.12	91	238.14		
222	87							

*Rare Earths:

La 57	Ce 58	Pr 59	Nd 60	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
138.92	140.13	140.92	144.27	—	152.0	157.3	159.2	162.46	163.5	167.64	169.4	173.5	175.0

Appendix IV

TABLE OF NATURAL STABLE ISOTOPES

<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Relative Abundance</i>	<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Relative Abundance</i>
H.....	1	1	99.98	S.....	16	32	97.0
		2	0.02			33	0.8
		3	(7×10^{-8})			34	2.2
He.....	2	4	100	Cl.....	17	35	76
Li.....	3	6	7.9			37	24
		7	92.1	A.....	18	36	0.34
Be.....	4	8	(0.05)			38	0.07
		9	99.95			40	99.59
B.....	5	10	20.00	K.....	19	39	93.2
		11	80.00			40	0.012
C.....	6	12	99.3			41	6.8
		13	0.7	Ca.....	20	40	96.76
N.....	7	14	99.62			42	0.77
		15	0.38			43	0.17
O.....	8	16	99.76			44	2.30
		17	0.04	Sc.....	21	45	100
		18	0.20	Ti.....	22	46	8.5
F.....	9	19	100			47	7.8
Ne.....	10	20	90.00			48	71.3
		21	0.27			49	5.5
		22	9.73			50	6.9
Na.....	11	23	100	V.....	23	51	100
Mg.....	12	24	77.4	Cr.....	24	50	4.9
		25	11.5			52	81.6
		26	11.1			53	10.4
Al.....	13	27	100			54	3.1
Si.....	14	28	89.6	Mn.....	25	55	100
		29	6.2	Fe.....	26	54	6.5
		30	4.2			56	90.2
P.....	15	31	100			57	2.8
						58	0.5

<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Relative Abundance</i>	<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Relative Abundance</i>
Co.....	27	59	100	Sr.....	38	86	10
Ni.....	28	58	68.1			87	6.6
		60	27.2			88	83.4
		(61)	(1.2)	Y.....	39	89	100
		62	3.8	Zr.....	40	90	48
		64	0.9			91	11.5
Cu.....	29	63	68			92	22
		65	32			94	17
Zn.....	30	64	50.4			96	1.5
		66	27.2	Cb.....	41	93	100.
		67	4.2	Mo.....	42	92	14.2
		68	17.8			94	10
		70	0.4			95	15.5
Ga.....	31	69	61.5			96	17.8
		71	38.5			97	9.6
Ge.....	32	70	21.2			98	23
		72	27.3			100	9.8
		73	7.9	Ru.....	44	96	5
		74	37.1			(98)	—
		76	6.5			99	12
As.....	33	75	100			100	14
Se.....	34	74	0.9			101	22
		76	9.5			102	30
		77	8.3			104	17
		78	24.0	Rh.....	45	103	100
		80	48.0	Pd.....	46	102	c
		82	9.3			104	a
Br.....	35	79	50			105	a
		81	50			106	a
Kr.....	36	78	0.42			108	a
		80	2.45			110	b
		82	11.79	Ag.....	47	107	52.5
		83	11.79			109	47.5
		84	56.85	Cd.....	48	106	1.5
		86	16.70			108	1
Rb.....	37	85	72			110	15.6
		87	28			111	15.2

<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Relative Abun- dance</i>	<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Relative Abun- dance</i>
		112	22.0	Ba.....56	135	5.9	
		113	14.7		136	8.9	
		114	24.0		137	11.1	
		116	6.0		138	74.1	
In.....49	113	4.5		La.....57	139	100	
	115	95.5		Ce.....58	140	89	
Sn.....50	112	1.1			142	11	
	114	0.8		Pr.....59	141	100	
	115	0.4		Nd.....60	142	36	
	116	15.5			143	11	
	117	9.1			144	30	
	118	22.5			145	5	
	119	9.8			146	18	
	120	28.5		Sm.....62	144	3	
	122	5.5			147	17	
	124	6.8			148	14	
Sb.....51	121	56			149	15	
	123	54			150	5	
Te.....52	122	2.9			152	26	
	123	1.6			154	20	
	124	4.5		Eu.....63	151	50.6	
	125	6.0			153	49.4	
	126	19.0		Gd.....64	155	21	
	128	32.8			156	23	
	130	33.1			157	17	
I.....53	127	100			158	23	
Xe.....54	124	0.08			160	16	
	126	0.08		Tb.....65	159	100	
	128	2.30		Dy.....66	161	22	
	129	27.13			162	25	
	130	4.18			163	25	
	131	20.67			164	28	
	132	26.45		Ho.....67	165	100	
	134	10.31		Er.....68	166	36	
	136	8.79			167	24	
					168	30	
Cs.....55	133	100			170	10	

<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Relative Abundance</i>	<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Relative Abundance</i>
Tm.....	69	169	100			196	a
Yb.....	70	171	9			198	c
		172	24	Au.....	79	197	100
		173	17	Hg.....	80	196	0.10
		174	38			(197)	(0.01)
		176	12			198	9.89
Lu.....	71	175	100			199	16.45
Hf.....	72	176	5			200	23.77
		177	19			201	13.67
		178	28			202	29.27
		179	18			203	0.006
		180	30			204	6.85
Ta.....	73	181	100	Tl.....	81	203	29.4
W.....	74	182	22.6			205	70.6
		183	17.3	Pb.....	82	(203)	
		184	30.2			204	1.5
		186	29.9			(205)	
Re.....	75	185	38.2			206	28.3
		187	61.8			207	20.1
Os.....	76	186	1.0			208	50.1
		187	0.6			(209)	
		188	13.4			(210)	
		189	17.4	Bi.....	83	209	100
		190	25.1	Th.....	90	232	100
		192	42.5	U.....	92	234	See text
Ir.....	77	191	33			235	See text
		193	67			238	See text
Pt.....	78	192	d	Values in parenthesis are doubtful or approximate. a, b, c, d are orders of abundance.			
		194	b				
		195	a				

Appendix V

ISOTOPIC MASSES

<i>Atomic Species</i>	<i>Atomic Number</i>	<i>Mass Number</i>	<i>Mass Value</i>	<i>Atomic Species</i>	<i>Atomic Number</i>	<i>Mass Number</i>	<i>Mass Value</i>
H.....1	1	1	1.00813	Ne		21	20.99968
H	2	2	2.01473	Ne		22	21.99864
H	3	3	3.01705	Na.....11	22	22	22.0002
He.....2	3	3	3.01711	Na		23	22.9961
He	4	4	4.00389	Na		24	23.9974
He	5	5	5.0137	Mg....12	24	24	23.9924
He	6	6	6.0208	Mg		25	24.9938
Li.....3	6	6	6.0186	Mg		26	25.9898
Li	7	7	7.01818	Mg		27	26.9921
Li	8	8	8.0251	Al.....13	26	26	25.9929
Be.....4	8	8	8.00792	Al		27	26.9899
Be	9	9	9.01504	Al		28	27.9903
Be	10	10	10.01671	Al		29	28.9904
B.....5	10	10	10.01631	Si.....14	27	27	26.9931
B	11	11	11.01292	Si		28	27.9866
B	12	12	12.01292	Si		29	28.9866
C.....6	11	11	11.01526	Si		30	29.9832
C	12	12	12.00398	Si		31	30.9862
C	13	13	13.00761	P.....15	30	30	29.9882
C	14	14	14.00763	P		31	30.9843
N.....7	13	13	13.01008	P		32	31.9841
N	14	14	14.00750	S.....16	32	32	31.9823
N	15	15	15.00489	S		34	33.978
N	16	16	16.011	Cl.....17	34	34	33.981
O.....8	15	15	15.0078	Cl		35	34.9803
O	16	16	16.000000	Cl		37	36.9779
O	17	17	17.00450	Cl		38	37.981
O	18	18	18.00369	A.....18	38	38	37.974
F.....9	17	17	17.0076	A		40	39.9750
F	18	18	18.0056	Cr.....24	52	52	51.948
F	19	19	19.00452	Ni.....28	58	58	57.942
F	20	20	20.006	Zn.....30	64	64	63.935
Ne.....10	20	20	19.99881	As.....33	75	75	74.934

<i>Atomic Species</i>	<i>Atomic Number</i>	<i>Mass Number</i>	<i>Mass Value</i>	<i>Atomic Species</i>	<i>Atomic Number</i>	<i>Mass Number</i>	<i>Mass Value</i>
Se.....	34	80	79.941	Te		128	127.936
Br.....	35	79	78.929	I.....	53	127	126.932
Br.....	—	81	80.926	Xe.....	54	134	133.929
Kr.....	36	78	77.926	Cs.....	55	133	132.933
Kr		80	79.926	Ba.....	56	138	137.916
Kr		82	81.927	Ta.....	73	181	180.927
Kr		83	82.927	W.....	74	184	184.00
Kr		84	83.928	Re.....	75	187	186.981
Kr		86	85.929	Os.....	76	190	189.981
Cb.....	41	93	92.926	Os		192	191.981
Mo....	42	98	97.946	Hg.....	80	200	200.016
Mo		100	99.945	Tl.....	81	203	203.036
Sn.....	50	120	119.912	Tl		205	205.037
Te.....	52	126	125.937				

Appendix VI

MOSTLY ABOUT NEUTRONS

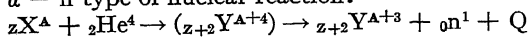
MASS OF THE NEUTRON

After Haymaker

<i>Reaction</i>	<i>Value</i>	<i>Investigator</i>
Boron + Alpha.....	1.0068	Chadwick
Boron + Alpha.....	1.0098-	
	1.012	Curie and Joliet
Magnesium + Alpha.....	1.0092	
Aluminum + Alpha.....	1.0089	Curie and Joliet
Beryllium + Alpha.....	1.0067+-	
	0.0001	Dunning
Impact Disintegration of		
Deuteron.....	1.0002	Lawrence and Livingston
Lithium + Deuteron.....	1.0063	L a u r i t z e n , Crane, et al
Lithium + Deuteron.....	1.0068	Ladenburg
Deuteron + Gamma(ThC'').....	1.0084-	
		Chadwick and Goldhaber
Deuteron + Gamma.....	1.00865	Feather

NEUTRON SOURCES

$\alpha - n$ type of nuclear reaction:



${}_4\text{Be}^9 + {}_2\text{He}^4 \rightarrow ({}_6\text{C}^{13}) \rightarrow {}_6\text{C}^{12} + {}_0\text{n}^1$	[1]
${}_3\text{Li}^7 + {}_2\text{He}^4 \rightarrow ({}_5\text{B}^{11}) \rightarrow {}_5\text{B}^{10} + {}_0\text{n}^1$	[2]
${}_5\text{B}^{11} + {}_2\text{He}^4 \rightarrow ({}_7\text{N}^{15}) \rightarrow {}_7\text{N}^{14} + {}_0\text{n}^1$	[3]
${}_7\text{N}^{14} + {}_2\text{He}^4 \rightarrow ({}_9\text{F}^{18}) \rightarrow {}_9\text{F}^{17} + {}_0\text{n}^1$	[4]
${}_9\text{F}^{19} + {}_2\text{He}^4 \rightarrow ({}_{11}\text{Na}^{23}) \rightarrow {}_{11}\text{Na}^{22} + {}_0\text{n}^1$	[5]
${}_{11}\text{Na}^{23} + {}_2\text{He}^4 \rightarrow ({}_{13}\text{Al}^{27}) \rightarrow {}_{13}\text{Al}^{26} + {}_0\text{n}^1$	[6]
${}_{12}\text{Mg}^{24} + {}_2\text{He}^4 \rightarrow ({}_{14}\text{Si}^{28}) \rightarrow {}_{14}\text{Si}^{27} + {}_0\text{n}^1$	[7]
${}_{13}\text{Al}^{27} + {}_2\text{He}^4 \rightarrow ({}_{15}\text{P}^{31}) \rightarrow {}_{15}\text{P}^{30} + {}_0\text{n}^1$	[8]
${}_{15}\text{P}^{31} + {}_2\text{He}^4 \rightarrow ({}_{17}\text{Cl}^{35}) \rightarrow {}_{17}\text{Cl}^{34} + {}_0\text{n}^1$	[9]
${}_{18}\text{Ar}^{40} + {}_2\text{He}^4 \rightarrow ({}_{20}\text{Ca}^{44}) \rightarrow {}_{20}\text{Ca}^{43} + {}_0\text{n}^1$	[10]

THE CAPTURE OF NEUTRONS

Capture Cross-Sections of Strongly Absorbing
Elements for Neutrons in Approximate
Thermal Equilibrium

<i>Atomic Species</i>	<i>$n \times 10^{24}, 27^\circ \text{C.}$</i>
3 Li.....	65
5 B.....	540
17 Cl.....	40
27 Co.....	35
45 Rh.....	125
47 Ag.....	55
48 Cd.....	3,000
49 In.....	300
62 Sm.....	4,260
63 Eu.....	3,400
64 Gd.....	22,200
66 Dy.....	1,200
67 Ho.....	340
75 Re.....	90
77 Ir.....	285
79 Au.....	90
80 Hg.....	450

BETA EMITTING ELEMENTS PRODUCED IN
URANIUM BY NEUTRONS

After Rasetti (1936), from Fermi

<i>Element, Z</i>	<i>Decay Period</i>	<i>Neutrons Used</i>
90 or 91.....	4 minutes	Slow
92.....	24 minutes	Slow
93.....	16 minutes	Fast
93.....	2.2 minutes	Fast and Slow
94.....	59 minutes	Fast and Slow
95 (?).....	10 seconds	?
96 (?).....	40 seconds	?
97 (?).....	12 hours	?

SOME TYPES OF NUCLEAR REACTIONS

After Rasetti

<i>Bombarding Particle</i>	<i>Emitted Particle</i>	<i>Z Becomes</i>	<i>A Becomes</i>
Alpha.....	Proton	$Z + 1$	$A + 3$
Alpha.....	Neutron	$Z + 2$	$A + 3$
Proton.....	—	$Z + 1$	$A + 1$
Proton.....	Alpha	$Z - 1$	$A - 3$
Proton.....	Neutron	$Z + 1$	A
Proton.....	Deuteron	Z	$A - 1$
Deuteron.....	Proton	Z	$A + 1$
Deuteron.....	Neutron	$Z + 1$	$A + 1$
Deuteron.....	Alpha	$Z - 1$	$A - 2$
Neutron.....	—	Z	$A + 1$
Neutron.....	Proton	$Z - 1$	A
Neutron.....	Alpha	$Z - 2$	$A - 3$

SOME NATURAL AND ARTIFICIAL RADIOELEMENT ANALOGS

Following is the interesting comparison of certain artificial radioelements that can be made with their natural analogs:

<i>Analogous Radioelement</i>	<i>Atomic Species</i>	<i>Radiation Emitted</i>	<i>Half Life</i>
Natural RaE.....	$_{83}\text{Bi}^{210}$	Beta	4.9 days
Artificial RaE.....	$_{83}\text{Bi}^{210}$	Beta	5.0 days
Natural radio- samarium.....	$_{62}\text{Sm}^?$	Alpha	1.2×10^{12} yrs.
Artificial radio- samarium.....	$_{62}\text{Sm}^?$	—	40 months
Natural radio- potassium.....	$_{19}\text{K}^{40}$	Beta	10^9 yrs.
Artificial radio- potassium.....	$_{19}\text{K}^{42}$	Beta	16 hours

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